UNIVERSITI PUTRA MALAYSIA

# *DETERMINATION OF Pb(II) AND Cr(VI) USING GOLD NANOPARTICLES AND IONOPHORE-MODIFIED SCREEN PRINTED ELECTRODE*

SALAMATU ALIYU TUKUR

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# DETERMINATION OF Pb(II) AND Cr(VI) USING GOLD NANOPARTICLES AND IONOPHORE-MODIFIED SCREEN PRINTED ELECTRODE

**By**

**SALAMATU ALIYU TUKUR**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science**

**November 2014**

This research work is dedicated to my loving husband and my

beloved parents

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Master of Science

# DETERMINATION OF Pb(II) AND Cr(VI) USING GOLD NANOPARTICLES AND IONOPHORE-MODIFIED SCREEN PRINTED ELECTRODE

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**SALAMATU ALIYU TUKUR**

**November 2014**

**Chair: Prof. Nor Azah Yusof, PhD**
**Faculty: Science**

In this research, gold nanoparticles (AuNPs) was prepared and used as modifier for disposable screen printed electrodes (SPE). The AuNPs was characterized by different spectroscopic techniques; prior to application on surface of the electrode to increase the sensitivity of the electrode.

The SPE was modified by casting AuNPs onto its surface. The modified electrode (AuNPs/SPE) was applied in Cr(VI) and Pb(II) detection. Linear sweep stripping voltammetry was performed with AuNPs/SPE and it showed better response than the bare SPE.

Analysis of chromium with AuNPs/SPE gave two linear calibrations and a lowest detection limit of $1.6 \times 10^{-6}$ µg $L^{-1}$ reported to date was achieved by applying deposition potential of -1.1 V and deposition time of 180 s. The electrode also showed very good recovery indicating the accuracy of the method. While concentration study of lead with AuNPs/SPE gave a linear calibration with $R^2$ = 0.990, a detection limit of 1.3 µg $L^{-1}$ was achieved by applying deposition potential of -1.2 V and deposition time of 240 s. Validation of the method with Inductively coupled plasma-mass spectroscopy (ICP-MS) and Atomic absorption spectroscopy showed very good correlation.

AuNPs together with an ionophore was also prepared and used as an electrode. The SPE was modified by casting the AuNPs/Ionophore solution. The AuNPs/ionophore/SPE was used for the analysis of Pb(II) and selective effect of the ionophore towards Pb(II). The ionophore used was found to be selective to lead ion in presence of foreign metal ions. This AuNPs/ionophore/SPE gave a lower LOD of 0.9 µg $L^{-1}$ which is lower than LOD of 1.3 µg $L^{-1}$ obtained with AuNPs/SPE. Selectivity study for a mixture of Hg(II) and Cd(II) ions with Pb(II), proves this sensor to be selective towards Pb(II).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk Ijazah Master Sains

**PENENTUAN Pb(II) DAN Cr(VI) MENGGUNAKAN SKRIN ELEKTROD TERUBAHSUAI DENGAN PARTIKEL NANO DAN EMAS DAN IONOFOR**

Oleh

**SALAMATU ALIYU TUKUR**

**November 2014**

**Pengerusi: Prof. Nor Azah Yusof, PhD**
**Fakulti: Sains**


Di dalam kajian ini, partikel nano emas (AuNPs) dihasilkan supaya menjadi pengubahsuai untuk skrin elektrod (SPE) pakai buang. AuNPs dicirikan menggunakan pelbagai teknik spektroskopi menerusi aplikasi AuNPs di atas permukaan elektrod untuk meningkatkan kepekaan elektrod.
SPE diubahsuai dengan melekatkan AuNPs ke atas permukaannya. Kemudian AuNPs/SPE telah digunakan di dalam pengesanan Cr(VI) dan Pb(II). Voltametri perlacatan linear telah dijalankan keatas AuNPs/SPE dan telah memberi hasil tindak balas yang baik berbanding analisis dengan elektrod tidak termodifikasi.

Analisis untuk kromium dengan AuNPs/SPE telah memberi dua penentukuran linear dan pengesanan terendah adalah $1.6 \times 10^{-6}$ µg $L^{-1}$ telah dicapai dengan menggunakan potensi pengenapan -1.1V and masa enapan selama 180 saat. Elektrod menunjukkan pemulihan yang baik menunjukkan ketepatan kaedah ini. Manakala kajian kepekatan plumbum dengan AuNPs/SPE memberikan penentukuran linear dengan $R^2 = 0.990$, had pengesanan 1.3 µg $L^{-1}$ telah dicapai dengan menggunakan potensi pengenapan -1.2 V dan masa pengenapan 240 s. Pengesahan secara kaedah spektroskopi plasma induktif (ICP-MS) dan spektroskopi penyerapan atom menunjukkan korelasi yang sangat baik.

AuNPs bersama-sama dengan ionofor juga telah disediakan dan digunakan sebagai pengubahsuai elektrod. Elektrod ini diubah dengan melekatkan AuNPs / Ionofor ke atas elekrod. AuNPs/Ionofor digunakan untuk menganalisa Pb(II) dan kesan selektif ionofor terhadap Pb(II). Ionofor yang digunakan didapati adalah selektif terhadap Pb(II) walaupun dalam kehadiran ion logam asing. Pengesan ini (AuNPs / ionophore / SPE) memberikan had pengesanan (LOD) lebih rendah 0.9 µg $L^{-1}$ berbanding dengan LOD 1.3 µg $L^{-1}$ yang didapati dengan AuNPs/SPE. Kajian pemilihan bagi campuran Hg(II) dan Cd(II) bersama Pb(II) membuktikan pengesan ini adalah selektif terhadap pengesanan plumbum.

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I certify that a Thesis Examination Committee has met on 10 November 2014 to conduct the final examination of Salamatu Aliyu Tukur on her thesis entitled "Determination of Pb(II) and Cr(VI) using Gold Nanoparticle and Ionophore-Modified Screen Printed Electrode" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| A | Absorbance |
| AdSV | Adsorptive stripping voltammetry |
| AgNPs | Silver nanoparticles |
| AuNPs | Gold nanoparticles |
| AuNs/CSPE | Gold nanostructures carbon screen printed electrode |
| BiNPs | Bismuth nanoparticles |
| BDD | Boron doped diamond |
| CCE | Carbon composite electrode |
| CE | Counter electrode |
| CNT | Carbon nanotubes |
| CV | Cyclic voltammetry |
| DPASV | Differential pulse anodic stripping voltammetry |
| DPV | Differential pulse voltammetry |
| Es | Standard reduction potential |
| GCE | Glassy carbon electrode |
| LOD | Limit of detection |
| LSV | Linear sweep voltammetry |
| MCNT | Multi-walled carbon nanotubes |
| NHAP | Nano sized hydroxyapatite |
| NPs | Nanoparticles |
| PH | Poly-L-Histidine |
| RE | Reference electrode |
| T | Transmittance |

| | |
|---|---|
| WE | Working electrode |
| SPE | Screen printed electrode |
| SWASV | Square wave anodic stripping voltammetry |
| SWV | Square wave voltammetry |

# CHAPTER ONE

# INTRODUCTION

## 1.1 Heavy Metals

Metals like cobalt, copper, iron, manganese, chromium and zinc are essential for metabolic processes at the recommended threshold, but can be toxic to living organisms when they exceed the threshold amount. Unfortunately metals such as lead, cadmium, mercury, arsenic are toxic even in trace amount. Due to their non-biodegradable nature, heavy metals are retained indefinitely in ecological system and in food chains. Additionally, their accumulation in body tissues causes serious damage to the human body parts (Aragay et al., 2012).

The main sources of heavy metal contamination can be from industries (release as dust due to industrial processes or waste release into rivers), agricultural activities, vehicle emission, and domestic activities. Studies of these metals pollution in the environment attributed the source of this pollution from anthropogenic and natural weathering (Hu et al., 2013), industrial activities and mining (Castillo et al., 2013, Nagarajan et al., 2013), continuous urbanization and industrialization in developing countries (Du et al., 2013). Heavy metal waste from industries and agricultural activities can accumulate into sludge, which may be applied to cultivated soil, and thereby could possibly be transfer into the food chain (Zhao et al., 2014).

Main exposure pathways of these metals can be through dermal absorption, ingestion and inhalation (Li et al., 2014), which may lead to occasional biological effects (Hu et al., 2013) especially in children (Du et al., 2013). And a well-known fact is that long term exposure to heavy metals causes' cancer (Li et al., 2014; Zhao et al., 2014). Heavy metal pollution is still threatening the environment and human health, because of their widespread in many areas; such as soil (Li et al., 2014), dust (Du et al., 2013) water and sediments (Hu et al., 2013; Castillo et al., 2013). Therefore, their control is paramount in respect of environmental and health improvement.

## 1.2 Problem Statement

Heavy metal impact on our environment and it's threat to human health makes monitoring of these metals a crucial to our present society. Thus, there is need for a fast, accurate and highly sensitive device that can easily detect these metal ions.

Heavy metal determination has been explored using a wide range of methods; Previously, methods like Laser-Induced Plasma Spectroscopy (Panne et al., 2001), Inductively Couple Plasma Mass/Optical Emission Spectroscopy (Pereira et al., 2010); and Electro-thermal Atomization Atomic Absorption Spectroscopy (Chaguaramus et al., 2012) has been used for determination of these metals but these methods are expensive and do not allow on site analysis due to non-portability of the equipment.

The advent of screen printed electrodes (SPE) and electrochemical methods which are inexpensive, portable and implore simple techniques, has drawn much interest and is the focus of researchers. While electrochemical techniques have paved way to reliable new methods, the issue of sensitivity is still a challenge. Generally nanoparticles especially metallic nanoparticle is receiving particular attention in sensor and biosensor application, for it's excellent conducting ability and capability in increasing sensitivity. Nanoparticles; have shown a great potential application in a wide range of existing and emerging technologies.

Metallic nanoparticles are used in heavy metals detection in order to avoid the previous used of mercury electrodes due to toxicity of mercury. Gold nanoparticles (AuNPs) in particular exhibit electronic, thermal, and optical properties, high catalytic properties, good biocompatibility, excellent conducting capability and high surface-to-noise ratio. Synthesis of AuNPs involves a very simple step using a reducing salt, unlike the long process involve in the synthesis of other metallic nanoparticles. Few methods were able to detect Cr(VI) to the micro level using gold film modified electrode (Torabi & Compton 2013); AuNPs modified SPE (Dom et al., 2008). Pb(II) was also detected to the micro level using functionalized mesoporous silica modified SPE (Sanchez et al., 2010); amino acid/AuNPs microelectrode (Costa et al., 2012); AuNS SPE (Wang et al., 2012). But in all the methods AuNPs was electrodeposited on the SPE, though electrodeposition method increases sensitivity, but involves memory loss; due to which the modification have to be repeated each time before taking the reading. Therefore drop-coating method can reduce the memory loss effect.

Selectivity is another important issue in heavy metals detection. Macrocyclic molecules as ionophore can be the solution to this problem, because it provides binding sites for suitable metal ions.

In this research, Pb(II) and Cr(VI) were detected down to nano level by electrochemical method using AuNPs modified SPE. The AuNPs has been synthesized by a simple method; where the chloroauric salt was reduced with sodium citrate under reflux at room temperature, and the AuNPs was drop-coated onto the SPE. Pb(II) was also detected down to nano level by electrochemical method using AuNPs/ionophore modified SPE. The ionophore for Pb(II) was prepared and mixed with AuNPs, then used to modify the SPE.

**1.3 Objectives**

The objective of this research is to develop a detection system for Pb(II) and Cr(VI) based on AuNPs modified SPE and AuNPs/Ionophore modified SPE.

Specific objectives for this research are

a) To prepare and characterize gold nanoparticles (AuNPs)

b).To electrochemically characterized screen printed electrode modified with AuNPs and ionophore

c) To evaluate the sensing capability of the modified screen printed electrodes in Pb(II) and Cr(VI) detection.

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