UNIVERSITI PUTRA MALAYSIA

MODIFICATION OF SCREEN PRINTED CARBON ELECTRODE WITH SILICON NANOWIRES FOR ELECTROCHEMICAL DETECTION OF Hg(II) AND Cd(II) IN WATER

SITI NUR ZAWANI BINTI MOHAMAD ZAIN

FS 2015 61

MODIFICATION OF SCREEN PRINTED CARBON ELECTRODE WITH SILICON NANOWIRES FOR ELECTROCHEMICAL DETECTION OF Hg(II) AND Cd(II) IN WATER

By

SITI NUR ZAWANI BINTI MOHAMAD ZAIN

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

May 2015

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

MODIFICATION OF SCREEN PRINTED CARBON ELECTRODE WITH SILICON NANOWIRES FOR ELECTROCHEMICAL DETECTION OF Hg(II) AND Cd(II) IN WATER

By

SITI NUR ZAWANI MOHAMAD ZAIN

May 2015

Chairman: **Ruzniza Mohd Zawawi, PhD**

Faculty: **Science**

Water pollution resulting from heavy metal ions such as mercury and cadmium tends to have lethal effects on the environment and living organisms. This indicates the need for further research to develop on heavy metal sensors that are fast, potable and cost effective. In this research, Silicon Nanowires (SiNW's), a 1-dimensional nanowire was used as a modifier for disposable screen printed carbon electrodes (SPCE) for detection of metal ions. The SiNW's was characterized by different spectroscopic techniques and the application of SiNW's on the surface of the electrode was found to increase the sensitivity of the electrode.

The screen printed carbon electrode was modified by casting SiNW's with 3-aminopropyl-triethoxysilane (APTES) onto the working electrode surface. The modified electrode (SiNW's/APTES/SPCE) was then applied for Hg^{2+} and Cd^{2+} ion detection. Electrochemical studies using linear sweep stripping voltammetry performed with SiNW's/APTES/SPCE were found to give a better response through the optimization of some analytical parameters.

Concentration study of mercury with SiNW's/SPCE gave linear calibrations and a detection limit value of 42.59 $\mu g\ L^{-1}$ was achieved by applying deposition potential of -1.2V and deposition time of 160s. The electrode showed very good recovery indicating the accuracy of the method, while concentration study of cadmium with SiNW's/SPCE gave a linear calibration with $R^2 = 0.994$. A detection limit of 251.7 $\mu g\ L^{-1}$ was also achieved by applying deposition potential of -1.2V and deposition time of 160s. Validation of the method with inductively coupled plasma-mass spectroscopy (ICP-MS) and atomic absorption spectroscopy showed very good correlation. This modified screen printed carbon electrodes with Silicon Nanowires (SiNW's/APTES/SPCE) also found for simultaneously detection of Hg^{2+} and Cd^{2+} ions in the solution.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untk ijazah Sarjana Sains

PENGUBAHSUAIAN ELEKTROD KARBON SKRIN TERCETAK DENGAN SILICON NANOWIRES(SiNW'S) UNTUK PENGESANAN ELEKTROKIMIA BAGI Hg(II) DAN Cd(II) DI DALAM AIR

Oleh

SITI NUR ZAWANI MOHAMAD ZAIN

Mei 2015

Pengerusi: **Ruzniza Mohd Zawawi, PhD**

Fakulti: **Sains**

Pencemaran air dengan ion logam berat seperti merkuri dan kadmium memberi kesan kepada persekitaran dan organisma hidup. Ini menunjukkan penyelidikan mengenai penderia logam berat yang memberi keputusan yang pantas, ringkas dan kos efektif adalah diperlukan. Dalam kajian ini, Silicon Nanowires(SiNW's) yang merupakan 1-dimensi dawai nano telah digunakan sebagai bahan pengubah suai untuk elektrod karbon skrin tercetak terpakai buang untuk mengesan logam berat ion. SiNW's telah di cirikan dengan menggunakan teknik spektroskopi, dan SiNW's diaplikasikan ke atas permukaan elektrod untuk meningkatkan kepekaan electrod tersebut.

Elektrod karbon skrin tercetak telah diubah suai dengan melekatkan SiNW's dengan APTES diatas permukaan elektrod kerja. Elektrod yang diubah suai (SiNW's/APTES/SPCE) telah diaplikasikan untuk mengesan Hg^{2+} dan Cd^{2+} ion. Kajian elektrokimia menggunakan voltametri sapuan linear pelucutan dilakukan menggunakan SiNW's/APTES/SPCE memberi kesan yang lebih baik dengan mengoptimumkan sebahagian parameter analisis.

Kajian kepekatan merkuri dengan SiNW's/APTES/SPCE telah memberikan penentukuran linear dan had pengesanan 42.59 $\mu g\ L^{-1}$ dengan menggunakkan potensi pemendapan -1.2V dan masa pemendapan selama 160s. Elektrod ini menunjukkan pengambilan semula yang baik yang menunjukkan ketepatan kaedah ini. Sementara kajian kepekatan kadmium dengan SiNW's/APTES/SPCE telah memberikan penentukuran linear dengan R^2 = 0.994. Had pengesanan 251.7 $\mu g\ L^{-1}$ telah dicapai dengan menggunakan potensi pemendapan -1.2V dan masa pemendapan selama 160s. Pengesahan kaedah ini dengan Spektrometriberat–induktif pasangan plasma (ICP-MS) dan spektroskopi serapan atom menunjukan korelasi yang sangat baik. Dengan elektrod karbon skrin tercetak dengan SiNW's (SiNW's/APTES/SPCE) ini juga didapati mampu untuk mengesan Hg^{2+} dan Cd^{2+} secara serentak.

ACKNOWLEDGEMENTS

Firstly, I would like to thanks to my supervisor and co-supervisor Dr. Ruzniza Mohd Zawawi and Prof Nor Azah Yusof for their encouragement and help. Without their help, guidance encouragement and knowledge I can't reach this state.

To my beloved parents, mama and ayah thank you so much support my journey to continue my study. Without them I can't achieved my dream. To my siblings thank you for financial support and advice. To my husband thank you so much for your fully support to me to finish this study.

To my friends and colleagues, izzah, k.emy, iffah, wani thank you for support and make me enjoying life at UPM. The enjoying time in UPM will be in my memory forever. Their encouragement to me to finish my study, love all of you. Special thanks farhana, zida, zira, salama always advise me and make me motivated to finish my journey in this study.

Best Regards

wawa

I certify that a Thesis Examination Committee has met on 11th May 2015 to conduct the final examination of Siti Nur Zawani Mohamad Zain on her thesis entitled Modification Of Screen Printed Carbon Electrode With Silicon Nanowires (SiNW's) For Electrochemical Detection Of Hg(II) And Cd(II) In Water 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.

Members of the Thesis Examination Committee were as follows:

Haslina Binti Ahmad, PhD
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zulkarnain B Zainal, PhD
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Yatimah Alias, PhD
Department of Chemistry
Faculty of Science
Universiti Malaya
(External Examiner)

ZULKARNIAN ZAINAL, PhD
Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 12 August 2015

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:

Ruzniza Mohd Zawawi, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Nor Azah Yusof, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

____

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in theUniversiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: ________________________ Date: __________________

Name and Matric No.: ____

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: ______________________
Name of
Chairman of
Supervisory
Committee: ______________________

Signature: ______________________
Name of
Member of
Supervisory
Committee: ______________________

Signature: ______________________
Name of
Member of
Supervisory
Committee: ______________________

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

A	Electrode surface area
APTES	3-aminopropyl-triethoxysilane
ASV	Anodic Stripping Voltammetry
AuNP	Gold nanoparticles
C	Concentration of analyte or reactant in the bulk solution
CNT	Carbon nanotubes
CSV	cathodic stripping voltammetry
CV	Cyclic Voltammetry
DPASV	Differintial Pulse Anodic Stripping Voltammetry
GCE	Glassy carbon electrode
I	Current
LSASV	Linear Sweep Anodic Stripping Voltammetry
MWCNT	Multi wall carbon nanotubes
N	Numbers of electrons
ppb	part per billion
ppm	part per million
SAM	Self-assembled monolayer
SiNW’s	Silicon Nanowire’s
SPCE	screen printed carbon electrode
SPE	screen printed electrode
SWASV	Square Wave Anodic Stripping Voltammetry
v	Scan rate
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Heavy Metals

Heavy metals are mostly defined by their chemical properties such as malleability, ductility with metallic luster and the ability to conduct heat and electricity as well as possessing the ability to lose its outer most electrons to form cations with basic oxides (John *et al*., 2002). They are group of metals with a high density which is greater than 5 gcm^{-3}. Heavy metals are known to form stable complexes or chelates with a variety of ligands and their average stability decreases with electronegativity of the metal in which they are attached to in the following order Pd > Cu > Ni > Co > Zn > Cd > Mn (Mellor *et al*., 1947, Irving *et al*., 1948). And several factors such as pH, are found to influence this order.

Heavy metal ions are regarded as the most toxic pollutants due to their acute toxicities, carcinogenicities and non-biodegradability. The main sources of heavy metal contamination are mostly contributed from metal related industries such as metal plating facilities, mining operations, fertilizer and electronic device manufactures, agricultural activities, vehicle emission, and domestic activities (Juang *et al*., 2002). The oxidation of the different metal species causes the solubility of the metal ions thus released into the surrounding environment through water drainages.

Wastes discharged from industrial and agricultural activities containing heavy metal can accumulate into sludge and drain down to cultivated soil; hence, this could easily be transferred into the food chain (Zhao *et al*., 2014). In many developing countries around the world, an increasing concentration of heavy metals in the environment is a serious problem to both human and animal health as well as protection and production of food stuffs.

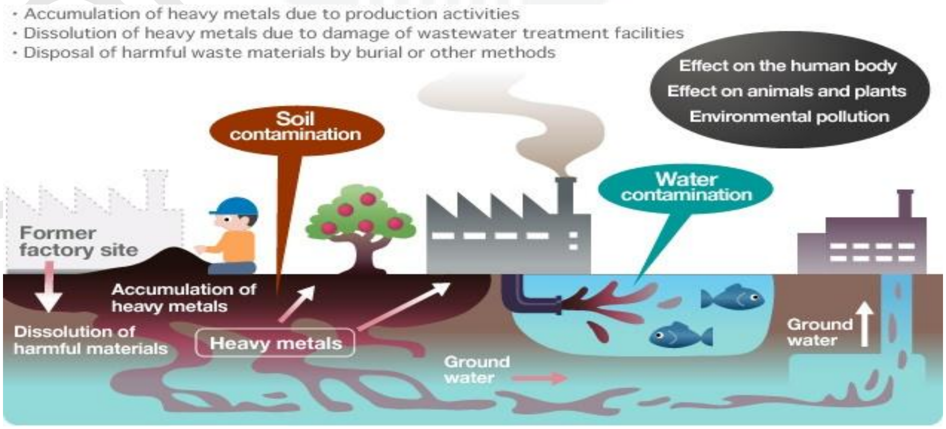

Figure 1.1: Source of Heavy Metal Pollution to Aqueous System (http://www.sagasiki-kankyo.co.jp)

Previous studies have proved that the use of spectroscopic techniques, such as inductively coupled plasma mass spectrometry (Hassan *et al*., 2004), surface-enhanced raman scattering (Enzhong *et al*., 2012) and cold vapour atomic fluorescence spectroscopy (Yu *et al*., 2005) in detecting the presence of this heavy metals can yield an accurate result. However, these techniques are highly costly because it requires expensive instruments, routine maintenance and specialized personnel in order to run the samples. These techniques also do not allow onsite analysis due to non-portability of the equipment.

For these reasons electrochemical sensors were developed and extensively being used in studying environmental pollution with diverse industrial applications. There is high demand of sensors in the world market that are easy to handle, compatible and can give a fast result. These sensors also offer advantages of low detection limits, a wide linear response range, good stability and reproducibility. Electrochemical sensor can be portable, simple to use,in-situ and miniature in size.These features are ideal for real time on field manaagement, thus the errors caused by the sample transportation and storage can largely be reduced (Cammann *et al*., 1996). The biochemical sensor usually consists of the analyte for example food sample, environmental sample or human sample and receptor that is specifically binded to the analyte, transducer element for example nanomaterial converted to an electronic signal by electrodes and amplified by a detector circuit using an appropriate reference and sent for processing to the computer software to be converted to a meaningful physical feature for example light, signal, and data display (Belluzo *et al*., 2007).

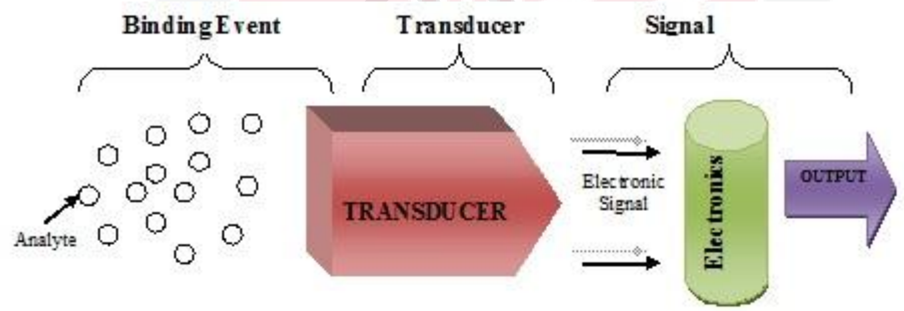

Figure 1.2: Schematic diagram of a bio/chemical sensor

The electroanalytical techniques that are usually employed in chemical sensor analysis includes; cyclic voltammetry(CV), differential pulse voltammetry (DPV), square wave voltammetry (SWV) and stripping voltammetry (SV). The stripping voltammetry is a sensitive electroanalytical technique used for the determination of trace amount of metals in a given solution. The technique consists of three steps. In the first step, metal ions are deposited onto an electrode which is held at a suitable potential. The solution is stirred during this step in order to maximize the amount of metal deposited. For the second step, stirring is stopped so that the solution will settles and finally in the third step, the metal deposits are stripped from the electrode by scanning the potential. The observed current during the stripping step can be used as an indirect measuremnt for the amount of metals in the solution.

The stripping step may consist of a positive or negative potential scan by creating either an anodic or cathodic current respectively. Hence, they are named as anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV). Anodic stripping voltammetry (ASV) has been recognized as a powerful technique for electrochemical measurements of trace metal ions in various samples of environmental, clinical, and industrial origin (Injang *et al*., 2010 , Yi *et al*., 2012) in particular due to its capability of preconcentrating analytes on the surface of the working electrode. It also allows quantification of heavy metal ions down to part per million (ppm) or even to part per billion (ppb) (Gu *et al*.,2013). Cyclic voltammetry (CV) is also widely used to study the presence of heavy metal but is not sensitive enough for environmental analysis never the less it is useful in optimization of analytical conditions (Buffle *et al*., 2005).

1.2 Screen Printed Electrode (SPEs)

The advent of disposable screen printed electrodes (SPEs) as an alternative to the conventional electrodes in development of analytical methods that respond to perform rapid 'in situ' analyses has become necesary due to many advantages it possess such as low cost, ease of handling and ease of preparation and moreover can be treated as disposable, thus avoiding the need for surface cleaning and the problem of memory effects.

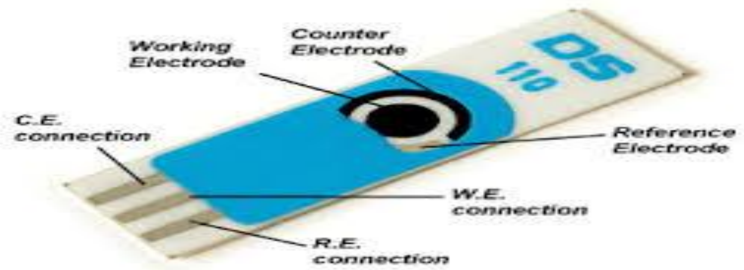

Figure 1.3: Screen printed carbon electrode consists of working electrode; counter electrode and reference electrode

The production of the SPEs comes with different ink on planar ceramic or plastic supports. SPEs can be modified by adding versatile substances of different nature such as nanomaterial, enzymes, self assembled monolayer (SAM), polymers and complexing agents (Honeychurch *et al*.,2012).

1.3 Problem Statement

Development of heavy metal ions detection and quantification in the environment is crucial to our present society. There is an increasing need for analytical systems that deliver fast and reliable data in the development of novel sensors. Sensitivity enhancement and lowering of the detection limit of heavy metal ions are the effort neede to be focused on.

Nanoparticles 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. Nanoparticles are used in heavy metals detection in order to avoid the previous used of mercury electrodes due to toxicity of mercury.

In this study SiNW's was used as the nanomaterial because it have excellent conducting capability and high surface-to-volume ratio to enhance the detection limit. Selectivity is another important issue in heavy metals detection. Macrocyclic molecules as ionophore can be the solution to this problem, because ionophore provides binding sites for interaction with metal ions. In this research, Hg^{2+} and Cd^{2+} were detected by electrochemical method using SiNW's modified SPCE. The detection limit of Hg^{2+} also much lower when modified SPCE with SiNW's/ionophore.

1.4 Objective of the studies

1.4.1 General Objective

The obective of this research is to develop a sensor for selective and specific detection and quantification of toxic metal ions such as Hg^{2+} and Cd^{2+} ions in environmental samples by utilizing silicon nanowires (SiNW's).

1.4.2 Specific Objective

1. To modify the screen printed carbon electrode (SPCE) for selective and specific detection of heavy metal ions Hg^{2+} and Cd^{2+} by utilizing silicon nanowires (SiNW's).
2. To optimize the deposition time, deposition potential, supporting electrolyte and characterize with SEM the modified SPCE.
3. To test the fabricate sensor on sea water samples.

REFERENCES

Abdul Rashid, J. I., Abdullah, J., Yusof, N. A., & Hajian, R. (2013). The Development of Silicon Nanowire as Sensing Material and Its Applications. *Journal of Nanomaterials*, 1–16.

Afkhami, A., Soltani-Felehgari, F., Madrakian, T., Ghaedi, H., & Rezaeivala, M. (2013). Fabrication and application of a new modified electrochemical sensor using nano-silica and a newly synthesized Schiff base for simultaneous determination of Cd(II), Cu^{2+} and Hg^{2+} ions in water and some foodstuff samples. *Analytica Chimica Acta*, *771*, 21–30.

Ahmar, H., Fakhari, A. R., Tabani, H., & Shahsavani, A. (2013). Optimization of electromembrane extraction combined with differential pulse voltammetry using modified screen-printed electrode for the determination of sufentanil. *Electrochimica Acta*, *96*, 117–123.

Bagheri, H., Afkhami, A., Khoshsafar, H., Rezaei, M., & Shirzadmehr, A. (2013). Simultaneous electrochemical determination of heavy metals using a triphenylphosphine/MWCNTs composite carbon ionic liquid electrode. *Sensors and Actuators B: Chemical*, *186*, 451–460.

Belluzo, M. S., Ribone, M. É., & Lagier, C. M. (2007). Assembling Amperometric Biosensors for Clinical Diagnostics. *Sensors*, *8*(3), 1366–1399.

Bi, X., Agarwal, A., Balasubramanian, N., & Yang, K.-L. (2008). Tripeptide-modified silicon nanowire based field-effect transistors as real-time copper ion sensors. *Electrochemistry Communications*, *10*(12), 1868–1871.

Buffle, J., & Tercier-Waeber, M.-L. (2005). Voltammetric environmental trace-metal analysis and speciation: from laboratory to in situ measurements. *TrAC Trends in Analytical Chemistry*, *24*(3), 172–191.

Cammmann,G. G., Guilbault,E. A., Hal, H. K., & Wolfbies,).O. S., The Cambridge Definition of Chemical Sensord, Cambridge Workshop in Chemical Sensors and Biosensors, Cambridge University Press: New York,1996.

Chen,Z., Pourabedi, Z., & Hibbert, D. B. (1999). Stripping Voltammetry of Pb(II), Cu(II), and Hg(II) at a Nafion - Coated Glassy Carbon Electrode Modified by Neutral Ionophores, *Microchimica Acta*, 964–96.

Compton, R. G., & Banks, C. E. (Eds.). (2007), *Cyclic Voltammetry at Macroelectrodes in Understanding Voltammetry*. Singapore: World Scientific Publishing Co. Pte Ltd.

Cui, Y. and C. M. Lieber (2001). Functional nanoscale electronic devices assembled using silicon nanowire building blocks. *Science* 291(5505), 851-853.

Domínguez Renedo, O., & Arcos Martínez, M. J. (2007). Anodic stripping voltammetry of antimony using gold nanoparticle-modified carbon screen-printed electrodes. *Analytica Chimica Acta*, *589*(2), 255–60.

Domínguez-Renedo, O., Ruiz-Espelt, L., García-Astorgano, N., & Arcos-Martínez, M. J. (2008). Electrochemical determination of chromium(VI) using metallic nanoparticle-modified carbon screen-printed electrodes. *Talanta*, *76*(4), 854–8.

Enzhong, T.; Penggang, Y.; Xiufeng, L.; Hongyan, Z.; Lin G. A novel surface-enhanced Raman scattering nanosensor for detecting multiple heavy metal ions based on 2-mercaptoisonicotinic acid functionalized gold nanoparticles. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2012, 97, 1007–1012.

Garcia, C. A. B.; Ju´ nior, L. R.; Neto, G. O. J. Pharm. Biomed. Anal. 2003, 31, 11–18.

Gu, T., Bu, L., Huang, Z., Liu, Y., Tang, Z., Liu, Y., … Luo, S. (2013). Dual-signal anodic stripping voltammetric determination of trace arsenic(III) at a glassy carbon electrode modified with internal-electrolysis deposited gold nanoparticles. *Electrochemistry Communications*, *33*, 43–46.

Hassan, K.; Mir, F.M.; Yadollah, Y.; Mojtaba, S. On-line reconcentration and simultaneous determination of heavy metal ions by inductively coupled plasma-atomic emission spectrometry. Analytica Chimica Acta 2004, 509, 89–94.

Hassan, S. S., Solangi, A. R., Kazi, T. G., Kalhoro, M. S., Junejo, Y., Tagar, Z. A., & Kalwar, N. H. (2012). Nafion stabilized ibuprofen–gold nanostructures modified screen printed electrode as arsenic(III) sensor. *Journal of Electroanalytical Chemistry*, *682*, 77–82.

He, X., Chen, L., Xie, X., Su, Z., Qin, C., Liu, Y., … Luo, Y. (2011). Square wave anodic stripping voltammetric determination of lead(II) using a glassy carbon electrode modified with a lead ionophore and multiwalled carbon nanotubes. *Microchimica Acta*, *176*(1-2), 81–89.

Hezard, T., Fajerwerg, K., Evrard, D., Collière, V., Behra, P., & Gros, P. (2012). Influence of the gold nanoparticles electrodeposition method on Hg(II) trace electrochemical detection. *Electrochimica Acta*, *73*, 15–22.

Hezard, T., Fajerwerg, K., Evrard, D., Collière, V., Behra, P., & Gros, P. (2012). Influence of the gold nanoparticles electrodeposition method on Hg(II) trace electrochemical detection. *Electrochimica Acta*, *73*, 15–22.

Honeychurch, K. C. (2012). Screen-printed Electrochemical Sensors and Biosensors for Monitoring Metal Pollutants. *Insciences Journal*, *2*, 1–51.

Ilaria Palchetti , Christa Upjohn, A. P. F. T. & M. M. (2000). Disposable Screen-Printed Electrodes (Spe) Mercury- Free for Lead Detection. *Taylor & Francis, 33*(7), 37–41.

Injang, U., Noyrod, P., Siangproh, W., Dungchai, W., Motomizu, S., & Chailapakul, O. (2010). Determination of trace heavy metals in herbs by sequential injection analysis-anodic stripping voltammetry using screen-printed carbon nanotubes electrodes. *Analytica Chimica Acta*, *668*(1), 54–60.

Injang, U., Noyrod, P., Siangproh, W., Dungchai, W., Motomizu, S., & Chailapakul, O. (2010). Determination of trace heavy metals in herbs by sequential injection analysis-anodic stripping voltammetry using screen-printed carbon nanotubes electrodes. *Analytica Chimica Acta*, *668*(1), 54–60.

Jiang, L., Wang, Y., Ding, J., Lou, T., & Qin, W. (2010). An ionophore–Nafion modified bismuth electrode for the analysis of cadmium(II). *Electrochemistry Communications*, *12*(2), 202–205.

John H. Duffus, (2002). HEAVY METALS - A MEANINGLESS TERM ? (IUPAC Technical Report) (IUPAC Technical Report), *74*(5), 793–807.

Juang, R.-S., & Shao, H.-J. (2002). A simplified equilibrium model for sorption of heavy metal ions from aqueous solutions on chitosan. *Water Research*, *36*(12), 2999–3008.

Kwon, D. H., An, H. H., Kim, H.-S., Lee, J. H., Suh, S. H., Kim, Y. H., & Yoon, C. S. (2011). Electrochemical albumin sensing based on silicon nanowires modified by gold nanoparticles. Applied Surface Science, 257(10), 4650–4654.

Laschi, S., Palchetti, I., & Mascini, M. (2006). Gold-based screen-printed sensor for detection of trace lead. *Sensors and Actuators B: Chemical*, *114*(1), 460–465.

Li, B. L., Wu, Z. L., Xiong, C. H., Luo, H. Q., & Li, N. B. (2012). Anodic stripping voltammetric measurement of trace cadmium at tin-coated carbon paste electrode. *Talanta*, *88*, 707–10.

Li, J., Guo, S., Zhai, Y., & Wang, E. (2009). Nafion–graphene nanocomposite film as enhanced sensing platform for ultrasensitive determination of cadmium. *Electrochemistry Communications*, *11*(5), 1085–1088.

Luo, X., Morrin, A., Killard, A. J., & Smyth, M. R. (2006). Application of Nanoparticles in Electrochemical Sensors and Biosensors. *Electroanalysis*, *18*(4), 319–326.

M. Brand, I. Eshkenazi, E. Kirowa-Eisnar, The silver electrode in square wave anodic stripping voltammetry. Determination of Pb(II) without removal of oxygen, Anal. Chem. 69 (1997) 4660–4664.

Mashhadizadeh, M. H., & Khani, H. (2010). Sol-Gel-Au nano-particle modified carbon paste electrode for potentiometric determination of sub ppb level of Al(III). *Analytical Methods*, *2*(1), 24.

Morton, J., Havens, N., Mugweru, A., & Wanekaya, A. K. (2009). Detection of Trace Heavy Metal Ions Using Carbon Nanotube- Modified Electrodes. *Electroanalysis*, *21*(14), 1597–1603.

P. Masawat, S. Liawruangrath, J.M. Slater, Flow injection measure- ment of lead using mercury-free disposable gold-sputtered screen- printed carbon electrodes (SPCE), Sens. Actuators B: Chem. 91 (2003) 52–59.

Pan, D., Wang, Y., Chen, Z., Lou, T., & Qin, W. (2009). Nanomaterial / Ionophore-Based Electrode for Anodic Stripping Voltammetric Determination of Lead : An Electrochemical Sensing Platform toward Heavy Metals, *81*(12), 5088–5094.

Pan, D., Wang, Y., Chen, Z., Yin, T., & Qin, W. (2009). Fabrication and Characterization of Carbon Nanotube-Hydroxyapatite Nanocomposite: Application to Anodic Stripping Voltammetric Determination of Cadmium. *Electroanalysis*, *21*(8), 944–952.

Philips, M. F., Gopalan, A. I., & Lee, K.-P. (2012). Development of a novel cyano group containing electrochemically deposited polymer film for ultrasensitive simultaneous detection of trace level cadmium and lead. *Journal of Hazardous Materials*, *237-238*, 46–54.

Rahman, N. A., Yusof, N. A., Amirah, N., Maamor, M., Mariam, S., & Noor, M. (2012). Development of Electrochemical Sensor for Simultaneous Determination of Cd (II) and Hg (II) Ion by Exploiting Newly Synthesized Cyclic Dipeptide, *7*(2017), 186–196.

Renedo, O. D., Alonso-Lomillo, M. a, & Martínez, M. J. A. (2007). Recent developments in the field of screen-printed electrodes and their related applications. *Talanta*, *73*(2), 202–19.

Rivas, G. a, Rubianes, M. D., Rodríguez, M. C., Ferreyra, N. F., Luque, G. L., Pedano, M. L., … Parrado, C. (2007). Carbon nanotubes for electrochemical biosensing. *Talanta*, *74*(3), 291–307.

Sanllorente-Méndez, S., Domínguez-Renedo, O., & Arcos-Martínez, M. J. (2010). Immobilization of acetylcholinesterase on screen-printed electrodes. Application to the determination of arsenic(III). *Sensors (Basel, Switzerland)*, *10*(3), 2119–28.

Shao, M., Ma, D. D. D., & Lee, S.-T. (2010). Silicon Nanowires - Synthesis, Properties, and Applications. *European Journal of Inorganic Chemistry*, *2010*(27), 4264–4278.

Somerset, V., Leaner,J., Mason, R., Iwuoha, E.,& Morrin, A.(2010).Development and application of a poly(2,2'-dithiodianiline) (PDTDA)-coated screen-printed carbon electrode in inorganic mercury determination. *Electrochimica Acta*, 55, 4240-4246.

Song, W., Zhang, L., Shi, L., Li, D.-W., Li, Y., & Long, Y.-T. (2010). Simultaneous determination of cadmium(II), lead(II) and copper(II) by using a screen-printed electrode modified with mercury nano-droplets. *Microchimica Acta*, *169*(3-4), 321–326.

Su, S., He, Y., Song, S., Li, D., Wang, L., Fan, C., & Lee, S.-T. (2010). A silicon nanowire-based electrochemical glucose biosensor with high electrocatalytic activity and sensitivity. Nanoscale, 2, 1704–1707.

Su, S., He, Y., Zhang, M., Yang, K., Song, S., Zhang, X., Lee, S. T. (2008). High-sensitivity pesticide detection via silicon nanowires-supported acetylcholinesterase - based electrochemical sensors. Applied Physics Letters, 93(2008),2006-2009.

Tahir, T. F., Salhin, A., Saad, B., & Ab Ghani, S. (2012). The 4-(Dimethylamino) benzaldehyde-4-ethylthiosemicarbazone as Ionophore for Mercury(II) Solid State Selective Electrode. *Electroanalysis*, *24*(6).

Tiean, G.; Lijuan, B.; Zhao, H.; Yan, L.; Zhiyong, T.; Ying, L.; Siyu, H.; Qingji, X.; Shouzhuo, Y.; Xinman, T.; Xubiao, L.; Shenglian, L. Dual-signal anodic stripping voltammetric determination of trace arsenic(III) at a glassy carbon electrode modified with internal-electrolysis deposited gold nanoparticles. Electrochemistry Communications 2013, 33, 43–46.

Uthaitip, I.; Peeyanun, N.; Weena S.; Wijitar D.; Shoji, M.; Orawon C. Determination of trace heavy metals in herbs by sequential injection analysis-anodic stripping voltammetry using screen-printed carbon nanotubes electrodes. Analytica Chimica Acta 2010, 668, 54–60.

Wei, Y., Yang, R., Yu, X.-Y., Wang, L., Liu, J.-H., & Huang, X.-J. (2012). Stripping voltammetry study of ultra-trace toxic metal ions on highly selectively adsorptive porous magnesium oxide nanoflowers. *The Analyst*, *137*(9), 2183–91.

Wei,Y., Gao, C., Meng, F., Li, H., Wang, L., Liu, J., & Huang, X. (2012). SnO 2 / Reduced Graphene Oxide Nanocomposite for the Simultaneous Electrochemical Detection of Cadmium (II), Lead (II), Copper (II), and Mercury (II): An Interesting Favorable Mutual Interference, (Ii), 1034–1041.

Wen, J.Y.; Yang, L.; Gu, R.; Hong, Q.L.; Nian, B.L. Determination of cadmium(II) by square wave anodic stripping voltammetry using bismuth–antimony film electrode. Sensors and Actuators B 2012, 166– 167, 544– 548.

Wonsawat, W., Chuanuwatanakul, S., Dungchai, W., Punrat, E., Motomizu, S., & Chailapakul, O. (2012). Graphene-carbon paste electrode for cadmium and lead ion monitoring in a flow-based system. *Talanta*, *100*, 282–9.

Y. Bonfil, M. Brand, E. Kirowa-Eisner, Trace determination of mercury by anodic stripping voltammetry at the rotating gold electrode, Anal. Chim. Acta 424 (2000) 65–76

Yan, S., He, N., Song, Y., Zhang, Z., Qian, J., & Xiao, Z. (2010). A novel biosensor based on gold nanoparticles modified silicon nanowire arrays. *Journal of Electroanalytical Chemistry*, *641*(1-2), 136–140.

Yi, W. J., Li, Y., Ran, G., Luo, H. Q., & Li, N. B. (2012). Determination of cadmium(II) by square wave anodic stripping voltammetry using bismuth–antimony film electrode. *Sensors and Actuators B: Chemical*, *166-167*, 544–548.

Yu, L.P. Cloud Point Extraction Preconcentration Prior to High-Performance Liquid Chromatography Coupled with Cold Vapor Generation Atomic Fluorescence Spectrometry for Speciation Analysis of Mercury in Fish Samples. J. Agric. Food Chem 2005, 53, 9656-9662.

Zheng, D., Vashist, S., Dykas, M., Saha, S., Al-Rubeaan, K., Lam, E., … Sheu, F.-S. (2013). Graphene versus Multi-Walled Carbon Nanotubes for Electrochemical Glucose Biosensing. *Materials*, *6*(3), 1011-1127.