



**Simultaneous Determination of Trace Levels of Cd(II) and Pb(II) in  
Tap Water Samples by Anodic Stripping Voltammetry with  
2-mercaptobenzothiazole Modified Electrode**

**Sophy Phlay**

**A Thesis Submitted in Partial Fulfillment of the Requirements for  
the Degree of Master of Science in Chemistry (Analytical Chemistry)**

**Prince of Songkla University**

**2019**

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**Thesis Title** Simultaneous Determination of Trace Levels of Cd(II) and Pb(II) in Tap Water Samples by Anodic Stripping Voltammetry with 2-mercaptobenzothiazole Modified Electrode

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I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

..... Signature

(Miss Sophy Phlay)

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<b>Thesis Title</b>	Simultaneous Determination of Trace Levels of Cd(II) and Pb(II) in Tap Water Samples by Anodic Stripping Voltammetry with 2-mercaptobenzothiazole Modified Electrode
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<b>Major Program</b>	Analytical Chemistry
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### ABSTRACT

Lead and cadmium in tap water can be toxic to human, even at low concentration. The determination of Cd(II) and Pb(II) is very important for environment and health.

In this work, in-situ modified Bi-Meso-MBT/GCE on glassy carbon electrode has been developed to determine Cd(II) and Pb(II) in tap water samples. This electrode was less toxic than mercury and mesoporous silica was used as a nanoparticle instead of nafion with the advantage of low cost. The metals were stripped off by square wave anodic stripping voltammetry (SWASV) under the optimized conditions.

The optimized conditions were in-situ preparation in acetate buffer pH 6.0, accumulation potential of -1.1 V, deposition time of 300 s and scan rate of 100 mV/s. The linear range of 5-50 ppb for both metals as well as LOD and LOQ of 0.56 ppb, 0.8 ppb and 1.87 ppb, 2.66 ppb for Cd(II) and Pb(II) were obtained respectively. The interaction between bismuth and MBT supports the performance of the modified electrode. The interference caused by cations including Ca(II), Mg(II), Zn(II), Mn(II), Fe(II), Cu(II) and Al(III) were found to provide not more than 5% signal change for both metals. The most interfering ion if present at high concentration is Cu(II) which can be masked by suitable and effective complexing agents.

This method was applied to tap water determination which was found within the range of 0.00 to  $0.06 \times 10^{-6}$  M for Cd(II) and 0.00 to  $0.05 \times 10^{-6}$  M for Pb(II) with standard addition method, lower than the permissible limit in edible portion of water (USEPA 0.015 M for Cd(II) and 0.005 M for Pb(II)) issued by the World Health Organization (WHO). Therefore, the Cd(II) and Pb(II) concentration in

tap water samples under the investigation is safe. The results from the proposed method were compared with those by ICP-OES using %recovery whereas standard addition and calibration curve method were compared by t-test. Both revealed to be not significantly different at 95% confident level.

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## LIST OF ABBREVIATIONS AND SYMBOLS

ASV	=	Anodic Stripping Voltammetry
AAS	=	Atomic Absorption Spectrometry
BDDE	=	Boron-doped Diamond Electrode
BDL	=	Below Detection Limit
Bi	=	Bismuth
CPEs	=	Carbon Paste Electrodes
DPASV	=	Differential Pulse Anodic Stripping Voltammetry
GCE	=	Glassy Carbon Electrode
ICP-OES	=	Inductive Coupled Plasma Optical Emission Spectrometer
LOD	=	Limit of Detection
LOQ	=	Limit of Quantification
Meso	=	Mesoporous Silica
MBSS	=	2-morpholinodithiobenzothiazole
MIOPs	=	Magnetic iron oxide nanoparticle
MBT	=	2-mercaptobenzothiazole
PVC	=	Polyvinyl Chloride
SWASV	=	Square Wave Anodic Stripping Voltammetry
SPE	=	Screen-Printed Electrodes
US EPA	=	United States Environmental Protection Agency
g	=	Gram
mV	=	Millivolt
mg/L	=	Milligram per Liter
µg/L	=	Microgram per Liter
$i_p$	=	Peak Current
BDL	=	Below Detection Limit
mM	=	Millimole per liter
ND	=	None Detected
RSD	=	Relative Standard Deviation
S/N	=	Signal to Noise Ratio
v/v	=	Volume by Volume



$\sigma$	=	The population standard deviation
WHO	=	World Health Organization

## Chapter 1

### Introduction

#### 1.1 Background

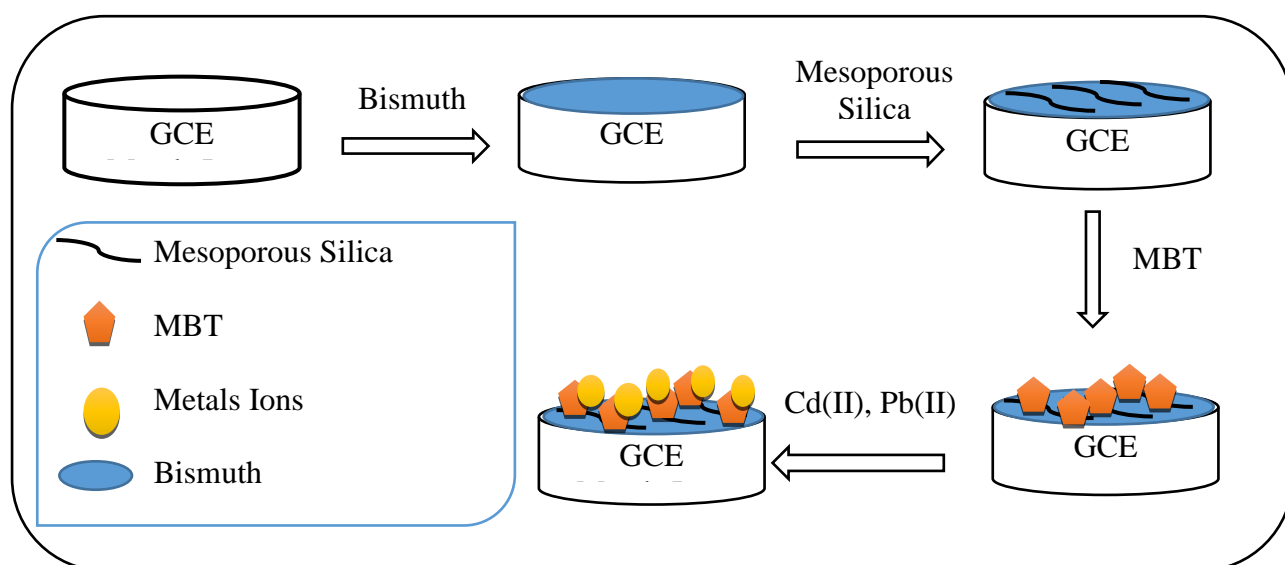
Water is one of important substances for people's life since it is used for consuming. Human organisms must receive certain amount of water every day. If an organism does not obtain the required amount of water for several days, it will die. It is obvious that the water consumed by the human organism should be pure. Water that contains any harmful bacteria or chemicals may cause various diseases of an organism or even death. There are many types of compounds to make water toxic such as heavy metals, biomass from factories or pesticides.

Thailand is the one of developed countries in Asia so water is also important for people's life. Songkhla is a province in southern Thailand. To the south it borders Kedah and Perlis of Malaysia. Hat Yai is a city in southern Thailand near the Malaysian border. It is the largest city of Songkhla Province, the largest metropolitan area in the south, and the third largest metropolitan area of the country. It is often mistaken as the provincial capital. Quality control for food and water is essential and the determination of heavy metals in water need to be clearly specified.

Most heavy metals are toxic, and their trace amounts can harm public health even at low concentration. In recent years, heavy metal pollution is considered to be one of the main sources of environmental problems, since it has severe toxicological effects on ecological systems. Heavy metals are widely distributed in nature and easily enter the food chain through a number of pathways, as well as tend to accumulate in living organisms causing various diseases and disorders to the human health. Moreover, it is a general collective term applied to the group of metals and metalloids with the atomic density greater than  $6 \text{ g/cm}^3$ . Although the term is only loosely defined but widely recognized and it is usually applied to the elements such as Cd, Cr, Cu, Hg, Pb and Zn which are commonly associated with pollutants and toxic problems. Among heavy metals with high potential in contaminating utility water are Cd(II) and Pb(II). Heavy metals occur naturally in rock-forming, or minerals water so there is a wide range of normal background concentrations of these metals in soils, sediments, water and living organism. For example, lead and cadmium ions may cause high blood pressure, kidney damage, nervous system damage among others,

which will be presented in detail in Topic 1.2. The problem is still found in the areas all over the world. Cadmium can be contaminated from battery whereas Pb(II) can contaminate water via the use of dye, paint, pipes and solder. It has been known that these metals can occur together and cause more damage especially to the brain (Karri, V *et al.*, 2016 and Clemow, Y. H *et al.*, 2015). In particular, lead(II) can result in irreversible neurological damage in children. United States Environmental Protection Agency (US EPA) has defined the maximum concentrations of lead and cadmium ions in drinking water to be 0.015 mg/l and 0.005 mg/l, respectively (<http://water.epa.gov>). Therefore, control and accurate determination of trace metals in environment is of paramount importance. The techniques which are cost effective, fast, simple and sensitive are therefore required in testing water samples. Modifying electrodes in electrochemical methods is currently under extensive investigations. It is based on putting active materials to collect metal ions for analysis. For example, in the case of glassy carbon, the principle is shown in Fig 1-1. First of all, bismuth is added on surface of glassy carbon to form alloys with Cd(II) and Pb(II). Secondly, mesoporous silica was added after Bi(III). The structure of mesoporous silica has a large number of pores with –OH group to increase the surface area. In the last step, 2-mercaptobenzothiazole has been added to interact with both metal ions.

**Fig 1-1** The principle of modification on glassy carbon surface.



## 1.2 Physical and Chemical Properties of Cd(II) and Pb(II)

Lead is a heavy metal which is classified to be in group IV of the periodic table. It is very soft, highly malleable, ductile, and is considered to be a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. A summary of physical properties is shown in Table 1-1.

**Table 1-1** Physical and chemical properties of Lead

Physical properties	Lead
Element symbol	Pb
Atomic number	82
Atomic mass	207.19
Atomic radiation	180 pm
Oxidation state	0, 2, 4
Melting point (S.T.P)	327 °C
Boiling point (S.T.P)	755 °C
Density (20 °C)	8.65 g/cm <sup>3</sup>
Electron configuration	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Young's modulus	16 GPa

Source: <https://en.wikipedia.org/wiki/Lead>

Cadmium is a chemical element with the symbol of Cd and the atomic number of 48. It is soft, bluish-white metal and is chemically similar to the two other stable metals in group 12 (zinc and mercury). A summary of the physical properties of Cadmium is presented in Table 1-2.

**Table 1-2** Physical and chemical properties of Cadmium

Physical properties	Cadmium
Element symbol	Cd
Atomic number	48
Atomic mass	112.41 g/mol

Oxidation state	0, 2
Atomic radius	151 pm
Melting point (S. T. P)	320.9 °C
Boiling point (S. T. P)	765 ± 2 °C
Density (20 °C)	8.65 g/cm <sup>3</sup>
Electron configuration	[Kr] 4d <sup>10</sup> 5s <sup>2</sup>
Young's modulus	15 GPa
Heat of fusion	4.77 kJ/mol
Heat of vaporization	179.5 kJ/mol

Source: <https://en.wikipedia.org/wiki/Cadmium>

### 1.2.1 Toxicology of Cadmium and Lead

A toxic heavy metal is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. Cadmium and Lead are highly toxic metals. Lead is a type of metal poisoning caused in the body and the brain is the most sensitive for lead. Involving symptoms may include abdominal pain, constipation, headaches, irritability, memory problems, inability to children, and tingling in the hands and feet. Lead causes almost 10% of intellectual disability of otherwise unknown cause and can result in behavioral problems. Furthermore, some of the effects are permanent. In several cases anemia, seizures, coma, or death may occur. For cadmium, it is a naturally occurring toxic heavy metal with common exposure in industrial workplaces, plant soils, and from smoking. Due to its low permissible exposure to humans, overexposure may occur even in situations where trace quantities of cadmium are found.

Cadmium and Lead can occur in a variety of source. Cadmium is used extensively in electroplating, although the nature of the operation does not generally lead to overexposure. Operations involving removal of cadmium paints by scraping or blasting may pose a significant hazard. Exposures to cadmium are addressed in specific standards for the general industry, shipyard employment, the construction industry, and the agricultural industry. Lead is present in tap water to some extent as a result of its dissolution from natural sources, but primarily from household plumbing systems in which the pipes, solder, fittings or service connections to homes contain

lead. Polyvinyl chloride (PVC) pipes also contain lead compounds that can be leached from them and result in high lead concentrations in drinking-water. The amount of lead dissolved from the plumbing system depends on several factors, including the presence of chloride and dissolved oxygen, pH, temperature, water softness and standing time of the water, soft, acidic water being the most plumb solvent. Lead is a general metabolic poison and enzyme inhibitor.

### **1.2.2 Sources and potential exposure of Cadmium and Lead**

Cadmium and lead can accumulate in the human body. Lead is also a common environmental pollutant. The causes of environmental contamination include industrial use of lead, such as that found in facilities that process lead-acid batteries or produce lead wire or pipes, and metal recycling and foundries. Lead can be exposed in blood, food, paint, soil, and water.

Lead is a naturally occurring toxic metal found in the Earth's crust. Its widespread use has resulted in extensive environmental contamination, human exposure and significant public health problems in many parts of the world. Important sources of environmental contamination include mining, smelting, manufacturing and recycling activities, and, in some countries, the continued use of leaded paint, leaded gasoline, and leaded aviation fuel. More than three quarters of global lead consumption is for the manufacture of lead-acid batteries for motor vehicles. Lead is, however, also used in many other products, for example pigments, paints, solder, stained glass, lead crystal glassware, ammunition, ceramic glazes, jewelry, toys and in some cosmetics and traditional medicines. Drinking water delivered through lead pipes or pipes joined with lead solder may contain lead. Much of the lead in global commerce is now obtained from recycling. People can become exposed to lead through occupational and environmental sources. This mainly results from: inhalation of lead particles generated by burning materials containing lead, for example, during smelting, recycling, stripping leaded paint, and using leaded gasoline or leaded aviation fuel; and ingestion of lead-contaminated dust, water (from leaded pipes), and food (from lead-glazed or lead-soldered containers).

Cadmium is a chemical element and a natural component of the earth's crust. Human activities can increase human exposure to cadmium through mining and combustion, which brings more cadmium into the air, water, and soil. Sources of

human exposure to cadmium in air, water, plants, animals, food, soil, and house dust are summarized below. For each source, likely magnitudes of human contact and the routes of contact inhalation, ingestion, and dermal contact are characterized. The primary use of cadmium is in the manufacturing of NiCd rechargeable batteries whereas that for cadmium is as a byproduct of refining zinc metal.

### **1.3 Anodic Stripping Voltammetry**

Anodic stripping voltammetry is a voltammetric method for quantitative determination of specific ionic species (Ha, K *et al.*, 2001). The analyte of interest is electroplated on the working electrode during a deposition step, and oxidized from the electrode during the stripping step. The current is measured during the stripping step. The oxidation of species is registered as a peak in the current signal at the potential at which the species begins to be oxidized. The stripping step can be linear, staircase, square wave, or pulse. Anodic stripping voltammetry usually incorporates three electrodes: a working electrode, auxiliary electrode (counter electrode), and reference electrode. The solution being analyzed usually has an electrolyte added to it. For most standard tests, the working electrode is a bismuth or mercury film electrode (in a disk or planar strip configuration). The mercury film forms an amalgam with the analyte of interest, which upon oxidation results in a sharp peak, improving the analyte resolution. In the case of the mercury film it is normally formed over a glassy carbon electrode. A mercury drop electrode has also been used for much the same reasons. In cases where the analyte of interest has an oxidizing potential above that of mercury, or where a mercury electrode would be otherwise unsuitable, a solid, inert metal such as silver, gold, or platinum may also be used. ASV is an established technology for sensitive and selective detection of metal ions and other electrochemically active substances but it can have several limitations. Firstly, the sample must be dissolved in supporting electrolyte. Secondly mercury was toxic. Next, the presence of background current in ASV measurement makes it difficult to detect the small stripping current associated with the oxidation of the analysis. Finally, ASV measures only redox-active species and processes, and the formation of intermetallic compounds between two different metals can disturb the individual stripping peaks. To help solve the problem, this work makes use of the modification of the GCE working electrode.

## **1.4 Working electrodes**

The working electrode is the electrode in an electrochemical system on which the reaction of interest occurs. The working electrode is often used in conjunction with an auxiliary electrode and a reference electrode in a three electrode system. Depending on whether the reaction on the electrode is a reduction or an oxidation, the working electrode is called cathode or anode, respectively. Common working electrodes can consist of materials ranging from inert metals such as gold, silver or platinum, to inert carbon such as glassy carbon, boron doped diamond or pyrolytic carbon, and mercury drop and film electrodes as mentioned before in Topic 1.3.

### **1.4.1 Glassy carbon electrode (GCE)**

Glassy carbon electrodes are prepared by means of a carefully controlled heating program of pre-modelled polymeric resin body in an inert atmosphere (Kamau, G.N *et al.*, 1998). Unlike many non-graphite carbons, it is impermeable to gases and also highly resistant to acid attack. The structure of glassy carbon consists of graphite planes randomly organised in a complex topology. Glassy carbon possesses isotropic properties and does not require a particular orientation in the electrode device. The performance of the electrode depends on the polishing materials and the procedures. Surface treatment is usually employed to create active and reproducible surface of the glassy carbon electrode and to enhance its analytical performance. Some additional activation steps have also been used to enhance the performance such as electro-chemical, chemical, vacuum heat, or laser treatment. The properties of carbonaceous materials depend on the manufacturing process. Carbonaceous electrodes have been used in biomedical fields because of their good conductivity, chemical inertness and mechanical stability.

### **1.4.2 Modified glassy carbon electrode**

Chemically modified electrodes are employed for the analysis of both organic and inorganic samples. Due to the fact of the toxicity of mercury, future regulations and occupational health considerations may severely restrict (or even ban) the use of mercury as an electrode material (Wang, J *et al.*, 2004). With electrode modification by organic compounds, polymers and nanomaterials, electrochemical



methods especially ASV can provide advantages including speed, accuracy, sensitivity, selectivity, reproducibility and stability among others. For simultaneous determination of Cd(II) and Pb(II), the most widely investigated is the use of bismuth to form alloys with both metals (Wu, Y *et al.*, 2008, Dongyue, L *et al.*, 2010) with satisfactory LOD especially when coupled by various materials to facilitate larger surface areas such as carbon nanotubes. In particular, GCE modified with bismuth, mesoporous silica and MBT were applied satisfactorily in the determination of both metals in water lily samples (Somkid, M *et al.*, 2017). A variety of compounds such as graphene (Xiao, L *et al.*, 2016), Co<sub>3</sub>O<sub>4</sub> (Zuo, Y *et al.*, 2017), polymers (Chamjangali, M *et al.*, 2015, Wu, Y *et al.*, 2008) and crown ether (Kaewkim, K *et al.*, 2013, Serrano N, 2015) were also found to be successful in preconcentrating both metal ions. Organic ligands with electron rich atoms including physc acid oxygen (Dai, H *et al.*, 2016, Huang, H *et al.*, 2016), phenolic oxygen and nitrogen (Kheirandish, S *et al.*, 2017), cysteine sulfur (Zhou, W *et al.*, 2016, Puy-Llovera, J *et al.*, 2017) and lysine nitrogen (Guo, Z *et al.*, 2017) were found to implement better analytical performances for Cd(II) and Pb(II) simultaneous determination. MBT is an alternative ligand containing nitrogen and sulfur (Khullar, I. P *et al.*, 1975) of which the derivative namely 2-mercaptobenzimidazole was comprehensively investigated in terms of structure of copper(II) complex (Tapachai, W *et al.*, 2017). The compound was used in extraction of both metals before analysis by FAAS (Tokalıoğlu, S *et al.*, 2017), as a biosensor for pesticides (Somerset, V. S *et al.*, 2006) and they can also form polymeric structure to accommodate more complexing sites (Sousa, M. d. F. B *et al.*, 1997). Its sensitivity to metals makes it one of the prominent modifying compounds for metal analysis. To lay the background on this, the modifications on the surface of glassy carbon electrode are shown here.

#### **1.4.2.1 Bismuth modified glassy carbon electrode**

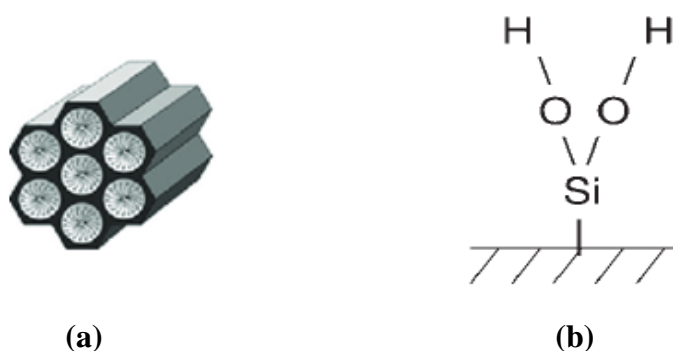
Bismuth coated carbon electrodes display an attractive stripping voltammetric performance which compares favorably with that of common mercury-film electrodes (Wang, J *et al.*, 2000). Bismuth is the most diamagnetic of all metals, and the thermal conductivity is lower than any metal except mercury. It has a high electrical resistance, and has the highest Hall Effect of any metal (that is, the greatest increase in electrical resistance when placed in a magnetic field). Bismuth is stable

for oxygen and water but dissolves in concentrated nitric acid. All bismuth salts form insoluble compounds when put into water. (Štěpánková, M *et al.*, 2017) A bismuth-film electrode prepared *ex situ* on the glassy carbon electrode support exhibited favorable electro analytical performance for voltammetric measurement of folic acid. Bismuth-film electrodes (BiFEs) have become an attractive configuration in electroanalysis as a potentially suitable replacement for mercury electrodes due to its environmentally friendlier nature. BiFEs present valuable electrochemical characteristics, such as a wide potential window in the cathodic range, negligible interference from dissolved oxygen, and most importantly, rather similar electrochemical behavior compared to mercury-based electrodes. BiFEs can be prepared by depositing a thin bismuth film on a suitable substrate material, such as the glassy carbon electrode (GCE) boron-doped diamond electrode (BDDE), carbon paste electrodes (CPEs), carbon fiber, screen-printed electrodes (SPE), or silver solid amalgam electrodes (AgSAE). (March, G *et al.*, 2015) The method for electroplating the electrode surface with bismuth is critical to obtaining satisfactory performances. Three methods exist to realize a bismuth deposit. The first method, *ex situ* plating, consists of electroplating the bismuth film before transferring the electrode into the sample solution for analysis. The plating conditions are variable but acidic media are recommended as bismuth ions are easily hydrolyzed as high pH. Plating solutions containing 5–200 mg/L Bi(III) are used with a deposition potential comprised between –0.5 and –1.2 V and deposition time of 1–8 min under conditions of forced convection (electrode rotation or convection). The second method, *in situ* plating, consists of adding directly Bi(III) ions in the concentration range 400–1000 mg/L into the sample solution. The bismuth film is deposited onto the electrode surface during the analysis. The main restriction of this method is the pH which must be fairly acidic, for the reason given above. The last method is essentially confined to carbon-paste electrodes. It is based on modifying the bulk of an electrode with bismuth compounds such as Bi<sub>2</sub>O<sub>3</sub>.

#### **1.4.2.2 Mesoporous silica modified glassy carbon electrode**

Mesoporous silica has been used to modify electrode popularly. This is mainly due to its unique properties such as ordered pore structures, very high specific surface areas and its possible synthesis in a wide range of morphologies such as

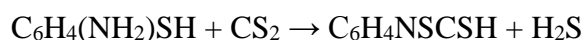
spheres rods, discs, powders, etc. Unlike traditional porous silica, mesoporous silica exhibits exceptionally ordered pores (Giraldo, L.F *et al.*, 2007). In addition, the rich silanol groups (SiOH) on their surfaces make them easily be modified with various functional groups, including NH<sub>2</sub>, SH, and S. Such functionalized mesoporous silica materials can strongly interact with metal ions, and hence have been employed as adsorbents (Xingxin, D *et al.*, 2014). Fig 1-2 (a) showed the structure of mesoporous silica and (b) showed the silanol group of mesoporous silica (Hoffmann, F *et al.*, 2006).



**Fig 1-2** (a) structure of Meso, (b) silanol groups present on the surface of mesoporous silica

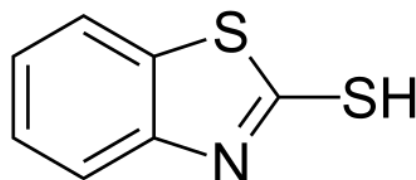
#### 1.4.2.3 2-mercaptobenzothiazole modified glassy carbon electrode

2-Mercaptobenzothiazole (MBT) is an organosulfur compound with the formula C<sub>6</sub>H<sub>4</sub>NSCSH. The molecule consists of a benzene ring fused to a 2-mercaptothiazole ring. It is used in the vulcanization of rubber. It is produced by the reaction of 2-aminothiophenol and carbon disulfide as shown below:



Other routes developed by Hoffmann included the reactions of carbon disulfide with 2-aminophenol and of sodium hydrosulfide with chlorobenzothiazole. Further synthetic advances were reported in the 1920s that included demonstration that phenyldithiocarbamates pyrolyze to benzothiazole derivative. It oxidizes to give the disulfide, which is called MBTS. Upon oxidation in the presence of secondary amines, it gives sulfenamide derivatives. One commercially useful example is 2-morpholinodithiobenzothiazole (MBSS), which is used as an accelerator in the vulcanization of rubber (Wikipedia, the free encyclopedia). 2-Mercaptobenzothiazole (MBT), or 2-benzothiazolethiol is a chelating agent that forms complexes with

different metal ions. An ethanolic solution of MBT could precipitate with ions of gold, silver, copper, lead and bismuth in an acidic or neutral solution (Jorn, C.C *et al.*, 2004).



**Fig 1-3** The structure of 2-Mercaptobenzothiazole (MBT)

Fig 1-3 shows the structure of 2-mercaptobenzothiazole. MBT is an organosulfur compound with the formula  $C_6H_4NSCSH$ . The molecule consists of a benzene ring fused to a 2-mercaptothiazole ring. The thiazole-based conjugated polymers with functional groups such as  $-NH_2$ ,  $-SH$  and  $-COOH$  in sensing biomolecules. The resulting 2-mercaptobenzothiazole modified GCEs (MBT/GCE) were used here for the determination of Cd(II) and Pb(II). The MBT modified GCE not only exhibits high electro-catalytic activities toward the electro oxidations of Cd(II) and Pb(II) with negatively shifted oxidation potentials and enhanced peak current responses, but also resolves the overlapped oxidation waves of Cd(II) and Pb(II) into two well-defined anodic peaks with enhanced current responses (Shervedani, R. K *et al.*, 2006). Thus, the simultaneous detections of Cd(II) and Pb(II) in water samples investigated as real sample applications should exhibit excellent sensitivity and reproducibility.

### 1.5 Literature review

Jureviciute and co-worker (2004) worked on the preparation of 2-mercaptobenzothiazole modified carbon paste electrode and its application to the stripping analysis of copper. In this work 2-mercaptobenzothiazole and silica modified on carbon paste electrode was used to determine copper ion with three steps: (1) Auto deposition of Cu at the open circuit potential, (2) solution exchange and adsorbate reduction and (3) linear sweep anodic voltammetry. In the work they used anodic voltammetric method within potential of  $0.34 \pm 0.05$  V vs Ag/AgCl and concentration of copper in range  $1 \times 10^{-7}$  to  $1 \times 10^{-6}$  mol  $L^{-1}$ . Linear dependence

between the anodic peak height and the analyte concentration in the solution has been obtained.

Lishuang and co-worker (2009) worked on glassy carbon electrode modified by electrochemical reduction of aromatic diazonium salts to determine Cd(II) and Pb(II). Glassy carbon electrode was modified by benzoic acid and electrochemical reduction of diazobenzoic acid. The anodic peak currents of cadmium and lead at benzoic acid modified by glassy carbon electrode were 7.2 and 6 times respectively compared to those at bare glassy carbon electrode. A linear range of Cd(II) and Pb(II) was observed at 0.5 – 50  $\mu\text{g/L}$  and detection limits were 0.20  $\mu\text{g/l}$  for Pb(II), 0.13  $\mu\text{g/l}$  for Cd(II). The relative standard deviations for six sequential measurements of 50  $\mu\text{g/l}$  Cd(II) and 50  $\mu\text{g/l}$  Pb(II) were 0.82% and 3.02%, respectively. Applicability of the sensor to the determination of Cd(II) and Pb(II) in sewerage samples was confirmed.

Parham and co-worker (2012) made use of on magnetic iron oxide nanoparticles to remove mercury from water sample modified by 2-mercaptobenzotiazole. Even though low concentration provides high toxicity and dangerous for human health, it can bio-accumulate in human body. 2-mercaptobenzotiazole as an adsorbent has been used to remove Hg(II) from dirty surface water modified by magnetic iron oxide nanoparticle. Preparation of adsorbent is easy and removal time was short. This recommended the method was fast, simple, cheap, effective and safe in controlling mercury from water polluting. Magnetic iron oxide nanoparticle (MIOPs) non-modifier could adsorb up to 43.46% of 50  $\text{ng/mL}$  of Hg(II) iron from contaminated water, the modifier could improve the efficiency up to 98.6 % for the same concentration. The time to complete ion removal was 4 min, NaCl has been used as an electrolyte. Capacity of adsorbent for mercury ion was found to be 590  $\mu\text{g/g}$ . This proposed method shows high potential for fast removal of Hg ion from water and wastewater with high efficiency.

Pourreza and co-worker (2014) used nano-TiO<sub>2</sub> modified with 2-mercaptobenzothiazole prior to flame atomic absorption spectrometry to determine Cd(II), Cu(II) and Pb(II). All metal ions have been adsorbed on nano-TiO<sub>2</sub>-MBT, eluted by nitric acid and determined by AAS. The factors affecting adsorption were considered. The calibration curves ranging from 0.2-25.0, 0.2-20.0, and 3.0-70.0

ng/mL have been used for optimization of cadmium, copper and lead, respectively. The limits of detection for Cd(II), Cu(II) and Pb(II) were 0.12, 0.15 and 1.38 ng/mL. The method was better or comparable for the determination of Cd(II), Cu(II) and Pb(II) in water and ore samples.

Teshome and co-worker (2013) modified bismuth on glassy carbon electrode to determine lead. Bismuth was been formed from plating solution 2 mmol/L Bi(NO<sub>3</sub>)<sub>3</sub> with 1 mol/L HCl at at -1.1 V (vs Ag/AgCl) and 300 s. Differential pulse anodic stripping voltammetry was used as a technique to determine lead in acetate buffer pH 5.0, within three ranges of concentration: 7.5 nmol/L to 0.1 μmol/L, 0.25 to 1 μmol/L and 2.5 to 12.5 μmol/L with coefficient of 0.991, 0.986 and 0.978. The detection limit as three times standard deviation from 7.5 nmol/L lead ( $n = 5$ ) was calculated to be 5.25 nmol/L utilizing a 5 min deposition time and sensitivity 83.97 nmol/mol. The proposed method provided good sensitivity and relatively safe from coexisting ions in excess amounts and can be used to determine lead in real sample.

Hwang and co-worker (2008) used bismuth modified carbon nanotube electrode (Bi-CNT electrode) to determine of lead, cadmium and zinc. The bismuth film has been prepared in-situ by plating onto the screen print CNT electrode. 0.1 mol/L (pH 4.5) acetate buffer has been used as buffer solution. Bismuth concentration, preconcentration time and rotation speed were optimized. Square wave anodic stripping voltammetry was selected. The modifier provided well defined, reproducible and sharp stripping signals. This work current increased linearly in the range from 2-100 μg/L with LOD of 1.3 μg/L lead, 0.7 μg/L for cadmium and 12 μg/L for zinc (S/N=3). This method was successfully applied to the analysis of these metals in environments.

Joseph and co-worker (2000) worked on the comparison between bismuth-coated and mercury-film electrode. Bismuth-film electrode was prepared by adding 400 μg/L (ppb) to sample and bismuth was deposited along with target metals on glassy carbon electrode. Stripping voltammetry measurements of microgram per liter levels of cadmium, lead, thallium, and zinc in nondeaerated solutions yielded well-defined peaks, along with a low background, following short deposition periods. In stripping voltammetry measurements at microgram per liter levels of cadmium, lead, thallium and zinc in nondeaerated solution yielded well-defined peak, along with

a low background, following short deposition periods. In addition, this method provided good LOD 1.1 – 0.3 ppb lead and followed with deposition time from 2-20 min. Changes in the peak potentials (compared to those observed at mercury electrodes) offer new selectivity dimensions. The bismuth was deposited on the carbon substrates to scanning electron microscopy sheds valuable comprehensions into the different morphologies by bismuth deposit on electrode. The growth pattern of bismuth film shed useful insight by scanning electron microscopy (SEM). The potential window was starting from -1.2 to -0.2 V was used for certificate quantitation of most metals measured at mercury electrode excepting of copper, antimony, and bismuth. A number of key experimental variables have been characterized and optimized to be responsible for high reproducibility from relative standard deviation 2.4 and 4.4 % for 22 repetitive determinations of 80 µg/L cadmium and lead. In this work, the development for further assessing the scope and power of bismuth electrodes and for understanding the role of the bismuth deposition on stripping was implemented. They explored the use of bismuth films for adsorptive stripping measurements of additional metals (that cannot be deposited) and for remote sensing of heavy metals in harsh environments. Preliminary results in these directions were very hopeful.

Shahryar and co-work (2011) presented excellent method for simultaneous determination of lead and cadmium by adsorptive differential pulse cathodic stripping voltammetry. This method was based on adsorptive accumulation of the complexes of Pb(II) and Cd(II) ions with 2-mercaptobenzothiazole onto hanging mercury drop electrode (HMDE), followed by the reduction species by differential pulse cathodic stripping voltammetry. The optimizations were obtained at pH 8.0, MBT  $1.0 \times 10^{-4}$  M, the accumulation potential of 0.4 V (vs Ag/AgCl), accumulation time of 160s, and the scan rate of 100 mV/s. Linear calibration curves have been established for the concentration of Pb(II) and Cd(II) in the range of 0.5-70 and 0.2-30 ng/mL, with the detection limit of 0.017 ng/mL for Pb(II) and 0.01 ng/mL for Cd(II). This method was successfully applied to determine of Cd(II) and Pb(II) ions in food samples.

From all literature review discussion above, 2-mercaptobenzothiazole modified glassy carbon electrode has been employed in different mixtures, e.g. 2-

mercaptobenzothiazole with mercury drop, nano-TiO<sub>2</sub> modified with MBT, etc. for electrochemical techniques for the determination of heavy metals. However, there are only a few reports about using bismuth 2-mercaptobenzothiazole with mesoporous silica nanoparticle in electrode modification. Normally, Nafion is one of the most extensively employed as strong bond reagent for silica nanoparticle coating but it is expensive. Therefore, in this analysis the possibility of using mesoporous silica as a strong adhesion reagent due to the fact that it is cheaper than Nafion. Here fabricated electrode of Bi-Meso-MBT/GCE was applied to determine of Cd(II) and Pb(II) in tap water samples.

## **1.6 Objectives**

- 1.6.1** To optimize the conditions for determining cadmium and lead in water sample by anodic stripping voltammetry with 2-mercaptobenzothiazole modified electrode
- 1.6.2** To investigate cadmium and lead concentration in water samples
- 1.6.3** To assess the quality of water whether it is suitable for utilization



## **Chapter 2**

### **Experimental**

#### **2.1 Chemicals and materials**

##### **2.1.1 Standard Chemicals**

- Cadmium nitrate stock standard solution 1000 mg/L (Carlo Erba, Italy)
- Lead nitrate stock standard solution 1000 mg/L (J.T. Baker, USA)
- Copper nitrate stock standard solution 1000 mg/L (Carlo Erba, Italy)
- Iron nitrate stock standard solution 1000 mg/L (J.T. Baker, USA)
- Nickel nitrate stock standard solution 1000 mg/L (J.T. Baker, USA)
- Zinc nitrate stock standard solution 1000 mg/L (J.T. Baker, USA)

##### **2.1.2 General chemicals and solvents**

- Mesoporous silica nanoparticle size 200 nm pore size 4 nm, (Sigma-Aldrich, Sudent)
- Bismuth(III) nitrate pentahydrate (Assay 98.0% min), AR grade (Fluka, Switzerland)
- Sodium acetate (Assay 99.8% min), AR grade (Ajax Finechem, Australia)
- Ultrapure water resistivity 18 M $\Omega$  obtained by passing deionized water through a ELGA water purification system (ELGA, England)
- Aluminum nitrate (Assay 98.0% min), AR grade (ASP, Australia)
- Calcium nitrate (Assay 99.0% min), AR grade (Ajax Finechem, Australia)

##### **2.1.3 Sample**

Tap water sample (Hat Yai, in the South of Thailand, approximately 30 km from Songkhla province; in February 2017). The samples were collected from eleven regions at Hat Yai city (APPENDIX C).

##### **2.1.4 NIST reference solution**

A reference material<sup>®</sup>, standard reference material (SRM), (1640, henceforth reference to as SRM 1640) was procured for testing from the National Institute of Standards and Technology (NIST). The standard contained certified amounts of metals as shown in Table 2-1 to 2-3.

**Table 2-1** Certified Mass Fraction

Element	$\mu\text{g.kg}^{-1}$	Element	$\mu\text{g.kg}^{-1}$
Aluminum	$52.0 \pm 1.5$	Cobalt	$20.28 \pm 0.31$
Antimony	$13.79 \pm 0.42$	Iron	$34.3 \pm 1.6$
Arsenic	$26.67 \pm 0.41$	Lead	$27.89 \pm 0.14$
Barium	$148.0 \pm 2.2$	Manganese	$121.5 \pm 1.1$
Beryllium	$34.97 \pm 0.41$	Molybdenum	$46.75 \pm 0.26$
Boron	$301.1 \pm 6.1$	Selenium	$21.96 \pm 0.51$
Cadmium	$22.79 \pm 0.96$	Silver	$7.62 \pm 0.25$
Chromium	$38.6 \pm 1.6$	Strontium	$124.2 \pm 0.7$
Vanadium	$12.99 \pm 0.37$		

Source: (Taylor, 1995)

**Table 2-2** Reference Mass Fraction

Element	$\mu\text{g.kg}^{-1}$	Element	$\text{mg.kg}^{-1}$
Copper	$85.2 \pm 1.2$	Calcium	$7.045 \pm 0.089$
Lithium	$50.7 \pm 1.4$	Magnesium	$5.819 \pm 0.056$
Nickel	$27.4 \pm 0.8$	Silicon	$4.73 \pm 0.12$
Potassium	$994 \pm 27$	Sodium	$29.35 \pm 0.31$
Rubidium	$2.00 \pm 0.02$		
Zinc	$53.2 \pm 1.1$		

Source: (Taylor, 1995)

**Table 2-3** Information Mass Fraction

Element	$\mu\text{g.kg}^{-1}$
Thallium	<0.1

Source: (Taylor, 1995)

## 2.2 Instruments and apparatus

### 2.2.1 Powerlab 2/20 Potentiostat

- Powerlab 2/20 Potentiostat (AD Instrument, Australia) with Echem software version 2.1.16 as shown in Fig 2-1.
- Computer system
- Nitrogen gas, High purity 99.99 %, (TIG, Thailand)

- 663 VA stand (Metrohm, Switzerland)

### **2.2.2. Inductively Coupled Plasma Optical Emission Spectrometer**

- Inductively Coupled Plasma Optical Emission Spectrometer, Optima 4300 DV (Perkin-Elmer, USA)

### **2.2.3 Electrochemical cell and electrode**

- Ag/AgCl (3 M KCl) used as reference electrode (Metrohm, Switzerland) as shown in Fig 2-2
- Glassy Carbon electrode used as working electrode as shown in Fig 2-2
- Platinum wire used as auxiliary electrode used as counter electrode (Number 6.1204.120, Metrohm, Switzerland) as shown in Fig 2-2
- 50 mL of electrode cell (Metrohm, Switzerland)

### **2.2.4 Apparatus**

- General glassware such as volumetric flasks 50,100, 250, 500, 1000ml and beaker 50,100, 500, 1000mL
- Hot plate EGO Model TC-254 (Denver Instrument, USA)
- Microliter pipette model : SL200 (20-200 $\mu$ L) from (Rainin, USA)
- Microliter pipette model : SL 1000 (100-1000 $\mu$ L) from (Rainin, USA)
- pH meter model 225 (Denver Instrument ,USA)
- Polyethylene bottle
- Polypropylene bottle
- Tissue paper

### **2.2.5 Materials**

- Alumina powder 0.05 micro diameter (Buehler, USA)
- 2-mercaptobenzothiazole (Sigma-Aldrich)
- Bismuth (III) nitrate pentahydrate (Fluka)
- Tetrabutylammonium hexafluorophosphate with the purity of  $\geq 98.0\%$
- Mesoporous silica (Sigma-Aldrich)



**Fig 2-1** Powerlab 2/20 Potentiostat



**GCE**  
(Working Electrode)



**Ag/AgCl**  
(Reference Electrode)



**Platinum Wire**  
(Auxiliary Electrode)

**Fig 2-2** electrochemical instrument and electrodes

## 2.3 Methodology

### 2.3.1 Preparation of stock standard solution

Stock standard solution was prepared from 1000 ppm and diluted to 1000 ppb Cadmium and Lead for corresponding solutions.

### 2.3.2 Working electrode preparation

Glassy carbon electrode was polished with alumina powder in sequence, and washed through doubly distilled water between each step of polishing.

The electrode was connected to potentiostat and placed on the stirring machine. The anodic stripping was applied to fully oxidize all metal in deposition step first before the next measurement. The polishing was performed when the electrode with contamination on surface was suspected.

### 2.3.3 Reference electrode

The electrode should be immersed in 3 M aqueous sodium chloride or potassium chloride. This electrode was removed from electrochemical cell and stored in this solution between experiments.

### 2.3.4 Optimization of operation conditions

The optimization was performed by varying parameter of interest while keeping others constant. The optimum values were used for all experiments. The experiment test was carried out with mixed stock solution of 20  $\mu\text{g/L}$  each Cadmium(II) and Lead(II). Stirring also has significant effected to current. In this work was used in speed 300 rpm. The parameters performed on from Powerlab 2/20 with Potentiostat software were summarized in Table 2-4.

**Table 2-4** Optimized condition for Powerlab 2/20 Potentiostat

Parameter	Studied Range
Deposition potential	-1 to (-1.5 V)
Deposition time	100 to 500 s
Effect of pH	pH 3 to 7
Bismuth concentration	100 to 500 $\mu\text{g/L}$
2-mercaptobenzothiazole concentration	100 to 600 $\mu\text{g/L}$
Mesoporous silica concentration	100 to 600 $\mu\text{g/L}$
Equilibration time	10 to 50 s
Step potential	1 to 20 mV
Pulse amplitude	25 to 80 mV
Scan rate	50 mV/s to 300 mV

#### 2.3.4.1 Selecting pulse wave form

Square wave anodic stripping voltammetry (SWASV) and differential pulse anodic stripping (SWASV) were optimized for determination of Cd(II) and

Pb(II) in tap water samples. The deposition time and the rest time of 20 µg/L Cd(II) and Pb(II) could be analyzed in 300 s and 30 s, respectively. The optimizing experiments were conducted by apply deposition potential at -1.4 V vs Ag/AgCl 3 M KCl. The method was applied to differential pulse anodic stripping voltammetry (DPASV) but it was found that the current signal did not appear until the deposition time was increase from 300s to 800 s. The current from SWASV was provide higher sensitivity than DPASV. Therefore, SWASV has been used for further experiment.

#### **2.3.4.2 Electrolyte**

pH of solution is very important because of effected on surface interaction. The variable value was performed with 0.1 M acetate (used as optimum condition). The experiment was run three times for each.

#### **2.3.4.3 Deposition potential**

To evaluate sensitivity in the voltammetric peak for different deposition potentials, the experiments were performed by mixed standard solution of 20 µg/L Cd(II) and Pb(II) with 0.1 M acetate buffer pH 6. The potential was varied from -1 to -1.5 V with Ag/AgCl reference electrode in stirring solution. Stripping voltamograms were recorded in square wave mode with under optimized conditions. The three replicates were performed for each potential.

#### **2.3.4.4 Deposition time**

The peak current was increased with increasing deposition time. The deposition time was investigated from 100 s to 500 s with deposition potential -1.1V in 20 µg/L of mixed metals solution under stirring condition with Ag/AgCl reference electrode.

#### **2.3.4.5 Scan rate and step potential**

The effect of scan rate on peak current was studied by varying from 50 mV/s to 250 mV/s. The concentration of Cd(II) and Pb(II) was 20 µg/L in 0.1 M acetate buffer pH 6. The step potential was increased from 1- 20 mV.

#### **2.3.4.6 Amplitude**

The amplitude was varied from 10 Hz to 80 Hz with 20µg/L of both metals in 0.1 M acetate buffer pH 6. The stripping peak was performed with the optimum conditions and three replications were performed for each.

#### **2.3.4.7 Equilibration time**

The equilibration time was studied in the range of 10s to 50s with 10 s increment. The optimum condition was carried out with 0.2 µg/L Cd(II) and Pb(II) in 0.1 M acetate buffer pH 6.

### **2.3.5 Analytical performance of ASV**

#### **2.3.5.1 Linear range**

Both metals (Cd(II) and Pb(II)) from stock standard solution was diluted with ultrapure water to obtain the concentrations 5 to 50 µg/L. Each concentration was analyzed in 50 mL of cell with Powerlab 2/20 Potentiostat at the optimum conditions. Linear range has been plot current with concentration. The current (y-axis) and concentration (x-axis) were plotted.

#### **2.3.5.2 Limit of detection (LOD) and Limit of quantification (LOQ)**

Limit of detection (according to IUPAC) is the small concentration or the lowest quantity of a substance that can be distinguished from the absence of absolute amount of analyte with a stated [confidence level](#). The LOD for ASV technique was analyzed by  $3\sigma/m$  (Uhrovčik, Jozef., 2004) where:

$\sigma$  = the standard deviation of 10 replications from 5 µg/L Cd(II) and Pb(II) added into blank solution

$m$  = the slope of the calibration curve

Limit of quantification (LOQ) was performed as the smallest concentration that can be quantified with precision and accuracy. LOQ is usually defined as signal to noise ratio (S/N) and also equivalent to 10 times of the standard deviation of noise ( $S/N = 10\sigma$ ). The LOQ is  $10\sigma/m$  where:

$\sigma$  = the standard deviation of 10 measurements from 5 µg/L of Cd(II) and Pb(II) added into blank solution

$m$  = the slope of the calibration curve

#### **2.3.5.3 Accuracy**

The accuracy of a measurement reflects how close a result comes to the true value. Determining the accuracy of a chemical analysis measurement requires calibration of the analytical method with a known standard. The accuracy of the method was studied by analyzing Standard Reference Material (SRM 1640). A portion of 10 mL SRM was diluted to 50 ml by using ultrapure water and added into

cell. The concentration of Cd(II) and Pb(II) was obtained by standard addition method using Powerlab 2/20 with Potentiostat. The results were compared with certified value and precision of the error was examined. The accuracy is the measurement of exact value of analyte concentration or agreement between measured value and certified value or an accepted reference value.

$$\% \text{Error} = \frac{(\text{Measured value} - \text{Real value})}{\text{Real value}} \times 100 \quad \dots\dots\dots 2.1$$

#### 2.3.5.4 Precision

Precision refers to how close two or more measurements are to each other, regardless of whether those measurements are accurate or not. Usually precision usually is expressed as a percentage of the relative standard deviation (%RSD) for statistically significant number of samples. It can be obtained by:

$$\% \text{RSD} = \frac{\text{SD}}{\bar{x}} \times 100 \quad \dots\dots\dots 2.2$$

Where:

SD = standard deviation of 10 measurements for 20  $\mu\text{g/L}$  of Cd(II) and Pb(II)

$\bar{x}$  = the mean value of 10 measurements for 20  $\mu\text{g/L}$  of Cd(II) and Pb(II)

#### 2.3.5.5 Recovery

Recovery is used to describe the relative percent error. Normally recovery presented in percent recovery (%R) and equation below:

$$\% \text{Recovery} = \frac{\text{Measured value}}{\text{Real value}} \times 100 \quad \dots\dots\dots 2.3$$

In this work %recovery was performed using tap water samples from the concentration 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50  $\mu\text{g/L}$  of Cd(II) and Pb(II).

#### 2.3.6 General procedure for determination Cd(II) and Pb(II)

This measurement was performed with three electrodes at room temperature. The SWASV experiments were performed with Powerlab 2/20 with Potentiostat. The cell consists of glassy carbon electrode as a working electrode, Ag/AgCl (3 KCl) as reference electrode and platinum wire as a counter electrode. All the stripping measurements were performed with 50 mL cell. pH was measured with Denver pH-meter (model 225) for all pH measurements. The standard solutions of Cd(II) and Pb(II) were added into the cell. The solution was stirred for 300 s and



stopped for 30 s. After that stripping voltamogram was obtained in range from -1.0 V to 0.0V, with the scan rate of 250 mV/s and pulse amplitude of 75 Hz.

## **2.4 Interferences**

The impact of common ions in water samples was evaluated with respect to their interference in the stripping peak of both metals by adding different concentrations of ions in 20 ppb of Cd(II) and Pb(II).  $Zn(NO_3)_2$ ,  $Ni(NO_3)_2$ ,  $Fe(NO_3)_2$ ,  $Co(NO_3)_2$ ,  $Ca(NO_3)_2 \cdot H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$  and  $MnCl_2 \cdot 4H_2O$  were used for interference study.

## **2.5 Application to tap water**

### **2.5.1 Sampling**

Tap water was collected from Hat Yai city in south of Thailand approximately 30 Km, from Songkhla, in 2017) and put in Polyethylene bottles ( the polyethylene bottles was cleaned by soaking with a 10%  $HNO_3$  solution overnight, and then rinsing at least three times with ultrapure water). The water samples were taken from the sampling sites around Hat Yai city by means of polyethylene bottle with volume between 1 and 1.5 L. Prior to the actual sampling, the bottle was filled with tap water and emptied several times. After that, it was left about half an hour before emptied with a fresh sample. The tap waters were collected from eleven regions at Hat Yai city after 15 min the opening of tap water. (Appendix C)

## Chapter 3

### Results and discussion

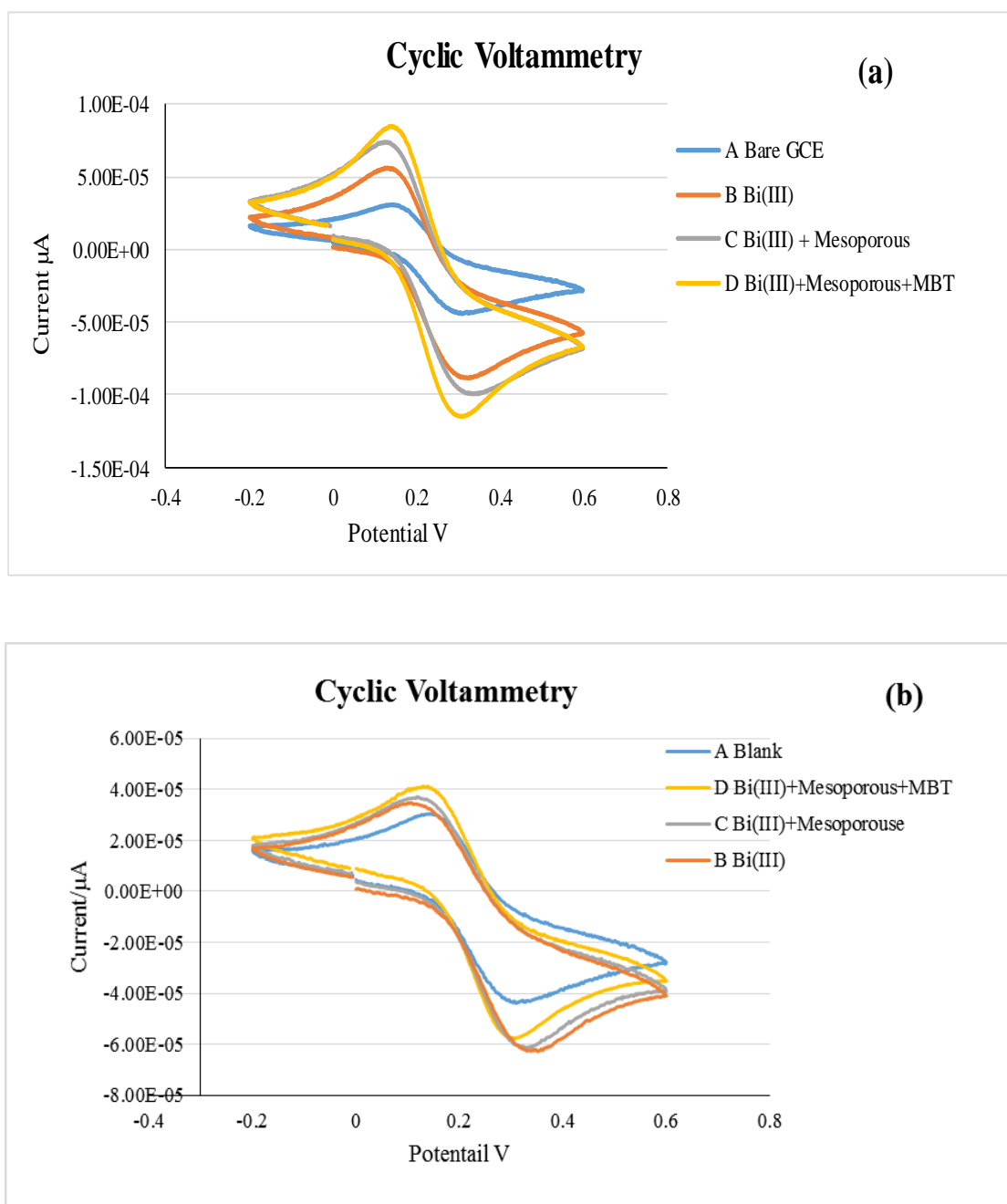
All the results to determine Cd(II) and Pb(II) in tap water sample performed by anodic stripping voltammetry modified with glassy carbon electrode are as shown:

#### 3.1 Optimization of Anodic stripping voltammetry parameter

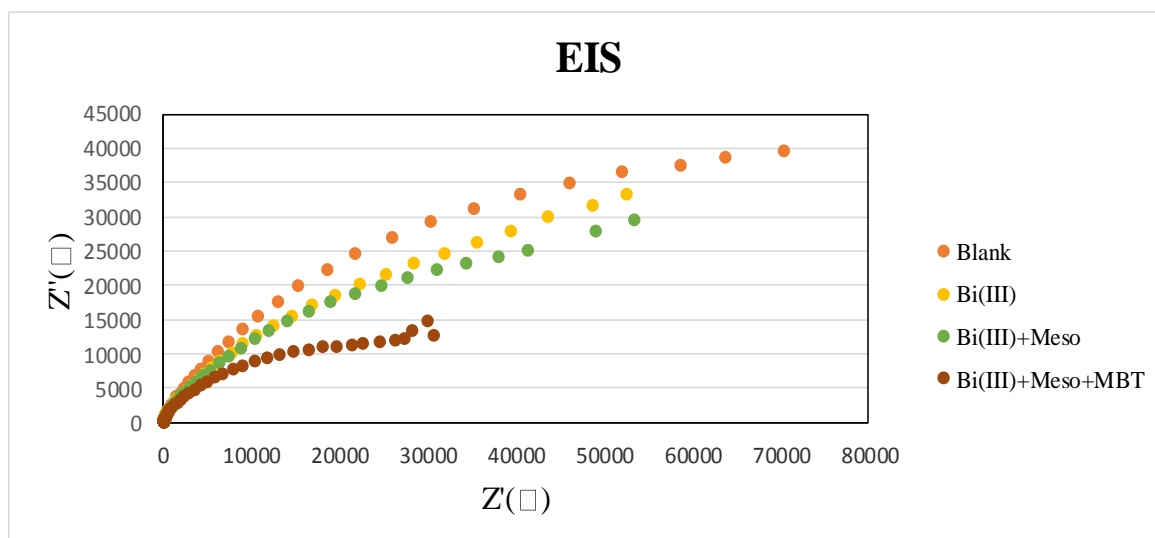
##### 3.1.1 Cyclic voltammetry of blank solution at glassy carbon electrode

Cyclic voltammetry was performed using 0.1 M acetate buffer pH 6.0 and the potential was scanned from - 0.2 to 0.6 V vs Ag/AgCl (3 M KCl) with scan rate 100 mV/s. Fig 3-1 showed the cyclic voltammetry (CV) of  $\text{Ru}(\text{NH}_3)_6^{3+}$  (a) and  $\text{Fe}(\text{CN})_6^{4-}$  (b) for the electrode at each step of modification. It is clear that the modified electrode work well with electron transfer for both inner sphere and outer sphere by maintaining reversibility along with increasing the current (Li, D *et al.*, 2010).

The electron transfer capacities of modified electrode were characterized by electrochemical impedance spectroscopy (EIS). Fig 3-2 reveals that the addition of each modifying agent help facilitate the electron transfer with less resistance, especially MBT (Zhao G *et al.*, 2016). Bare glassy carbon and modified electrode were observed to have different semicircle. The smaller semicircle reflects the lower the resistance provide by the modified electrode.



**Fig 3-1** (a) Cyclic Voltammometry for Bare GCE (A), Bi/GCE (B), Bi-Meso/GCE (C) and Bi-Meso-MBT/GCE (D) with scan rate  $100\text{mV/s}$  in  $2.5\text{ mM Ru}(\text{NH}_3)_6^{3+}$  in  $0.1\text{ M}$  acetate buffer and in picture (b)  $2.5\text{ mM K}_4\text{Fe}(\text{CN})_6$

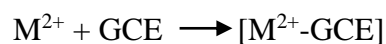


**Fig 3-2** Nyquist plots of the (A) GCE, (B) Bi/GCE (C), Bi-Meso/GCE, (D) Bi-Meso-MBT/GCE in 0.1 M acetate buffer.

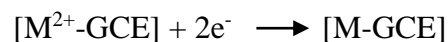
### 3.1.2 Operational principle of stripping voltammetry determination Cd(II) and Pb(II) on the glassy carbon electrode

The principle of Cd(II) and Pb(II) determination using modified electrode (Bi-Meso-MBT/GCE) involved the following steps (Vasanthi, S *et al.*, 2017). Both metal ions are preconcentrated on electrode for 300 s. After metals were reduced for 30 s then they were stripped on electrode in potential range -1.0 V to 1.0 V. (For Pb(II) the same reactions apply)

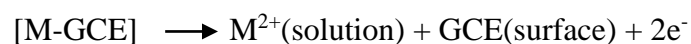
#### 1. The preconcentration through complexation in 0.1 M acetate buffer pH 6 for 300 s



#### 2. Reducing step in 0.1 M acetate buffer (pH 6) at -1.1 V for 30 s



#### 3. For stripping process in potential range -1.0 V to 1.0 V in acetate buffer pH 6



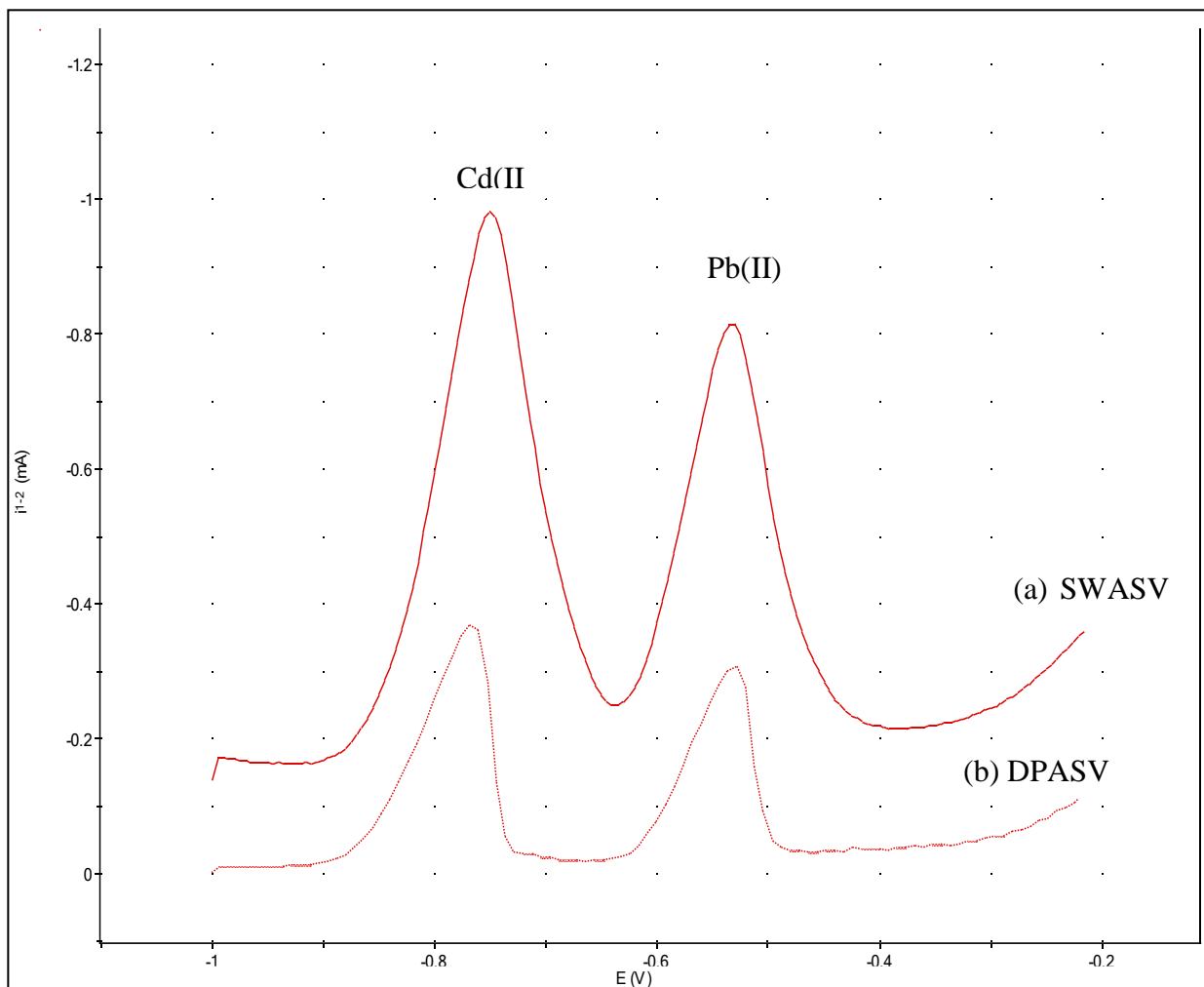
(M are Cadmium and Lead)

### 3.1.3 Comparison of Pb(II) and Cd(II) stripping voltamogram from square wave and differential pulse

Square wave anodic stripping and differential pulse anodic stripping signals were compared. In Table 3-1, for stripping current at 20 ppb of Cd(II) and Pb(II) in different modes with Bi-Meso-MBT/GCE with different deposition time, step potential and amplitude. The current from SWASV was clear to have higher sensitivity than current DPASV as shown in Fig 3-3. Even at greater deposition time, the current from DPASV has less sensitivity so SWASV was chosen for all further experiments in this work.

**Table 3-1** SWASV and DPASV parameters

<b>Parameter</b>	<b>SWASV</b>	<b>DPASV</b>
<b>Accumulation step</b>		
Deposition potential	-1000 mV	-1000mV
Deposition time	300s	800s
Equilibration time	30s	30s
<b>Measuring Step</b>		
Frequency	50Hz	-
Step potential	160mV	100mV
Amplitude	75mV	75mV

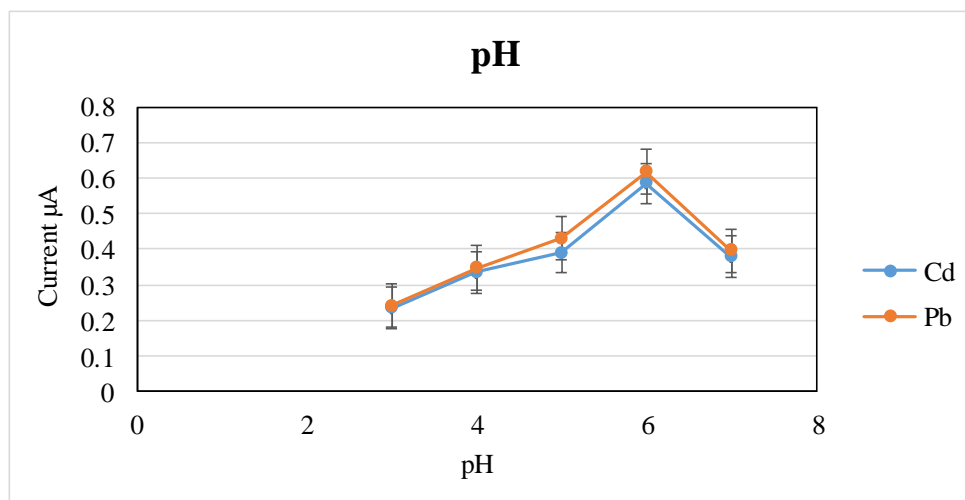


**Fig 3-3** Comparison of currents of 0.1 mg/L Cd(II) and Pb(II) from (a) SWASV (b) DPASV with the conditions as specified in the text.

### 3.1.4 The optimum conditions

#### 3.1.4.1 Effect of pH

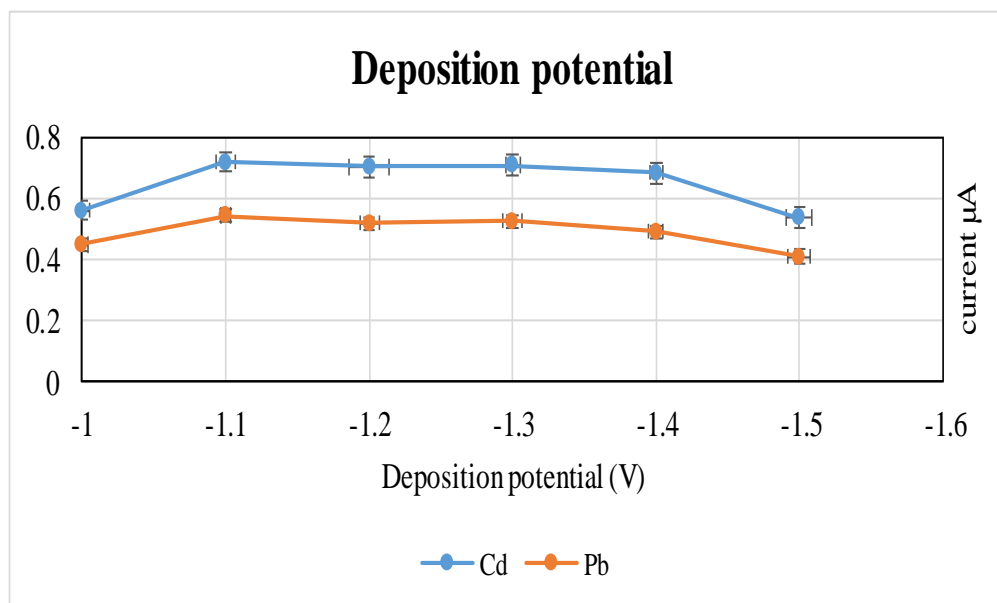
With the experimented pH range of 1.0 to 7.0, the maximum peak current was obtained at pH 6.0 and this value was used for the next investigations as shown in Fig 3-4. This pH is suitable for the formation of a sulfide anion to form complexes with metal ions corresponding with its pK<sub>a</sub> of 6.93 obtained from: (<http://www.chemicaland21.com/specialtychem/perchem/2-mercaptobenzothiazole.htm>). If pH is lower than 6.0, protonation causes the formation of sulfhydryl group which makes it more difficult for complex formation. At pH higher than 6.0, the metals are probably susceptible to form hydroxides.



**Fig 3-4** Effect of pH of 20 µg/L Cd(II) and Pb(II) in 0.1 M acetate buffer with SWASV

#### 3.1.4.2 Effect of deposition potential

The deposition potentials were investigated over a potential range of -0.1 to -1.5 V. As shown in Fig 3-5, at the beginning the current increased steeply up to -1.1 V and became constant. This is due to greater extent of metal accumulation until the potential was high enough for both metals. Beyond potential at -1.4 V, the current started to drop, possibly because greater thickness slows down the mass transfer and higher negative potential is susceptible to side reactions (Yang, D *et al.*, 2014). The highest current for both metals was found at -1.1 V which was fixed for metal electro deposition for following studies.

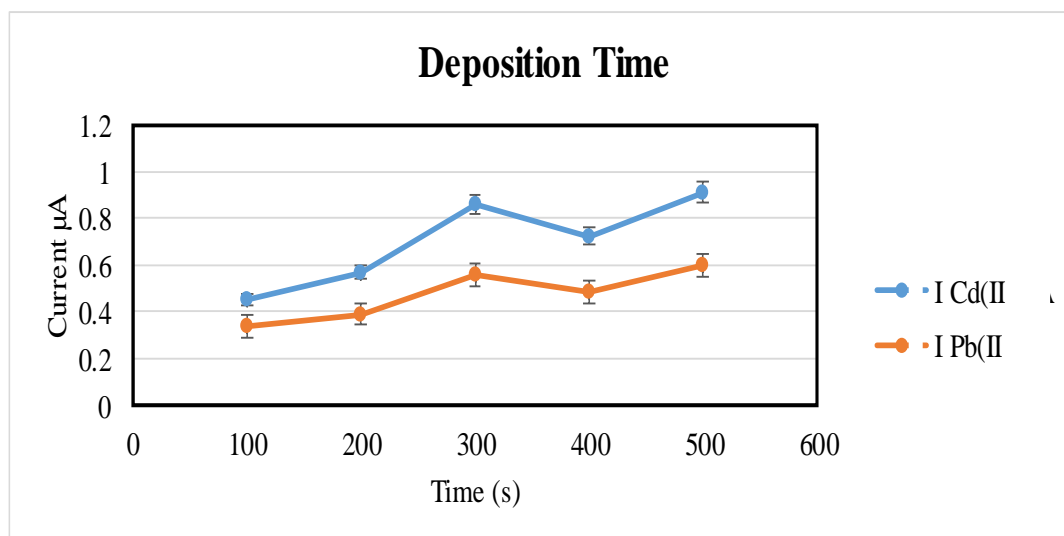


**Fig 3-5** Effect of deposition potential with SWASV pH 6 of 20 µg/L Cd(II) and Pb(II) in 0.1 M acetate buffer.

#### 3.1.4.3 Effect of deposition time

The deposition time was experimented from 100 to 500 s. As shown in Fig 3-6, the current gradually increased with time up to 300 s because greater accumulation of bismuth facilitated alloy forming until surface saturation was reached. However, the current dropped before went up again a little, reflecting that the time is needed for alloy rearrangement. The highest peak current was found at 300 s as shown in Fig 3.5 and this was used for further optimizations as well as applications (Zhu, Y *et al.*, 2017).

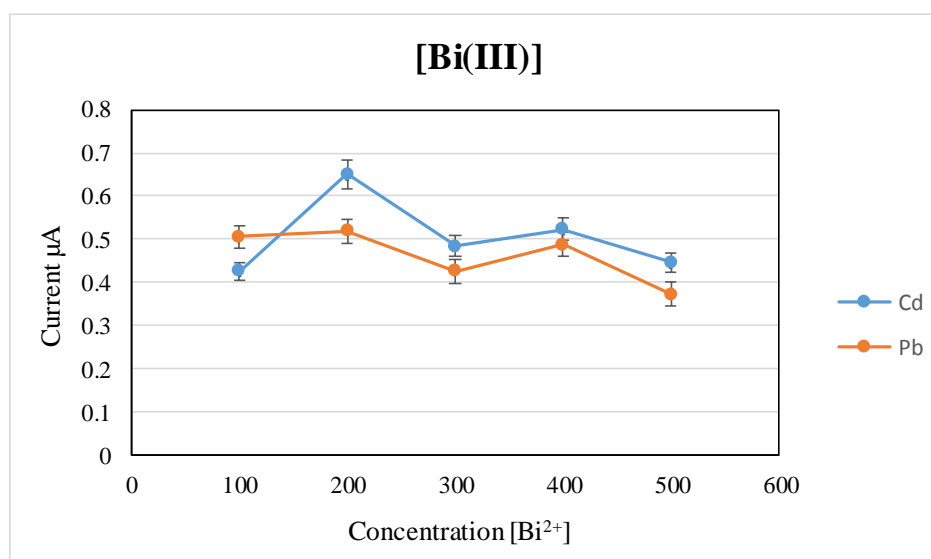




**Fig 3-6** Effect of deposition time with SWASV of 20 µg/L Cd(II) and Pb(II) in 0.1 M acetate buffer.

#### 3.1.4.4 Effect of Bismuth concentration

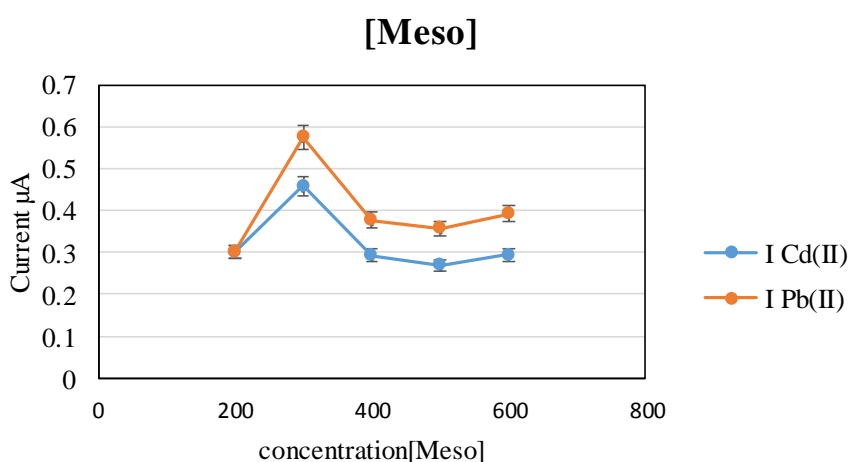
The concentrations of Bi(III) was varied from 100 to 500 µg/L. Fig 3-6 revealed normal trend of increasing due to the increase of film thickness and then decreasing because greater thickness can inhibit the mass transfer during stripping step (Xiao, L *et al.*, 2014). The concentration of 200 µg/L provided the greatest peak current for both metals and was therefore selected for following experiments.



**Fig 3-7** Effect of Bi(III) with SWASV of 20 µg/L Cd(II) and Pb(II) pH 6 in 0.1 M acetate buffer.

### 3.1.4.5 Effect of Mesoporous Silica concentration

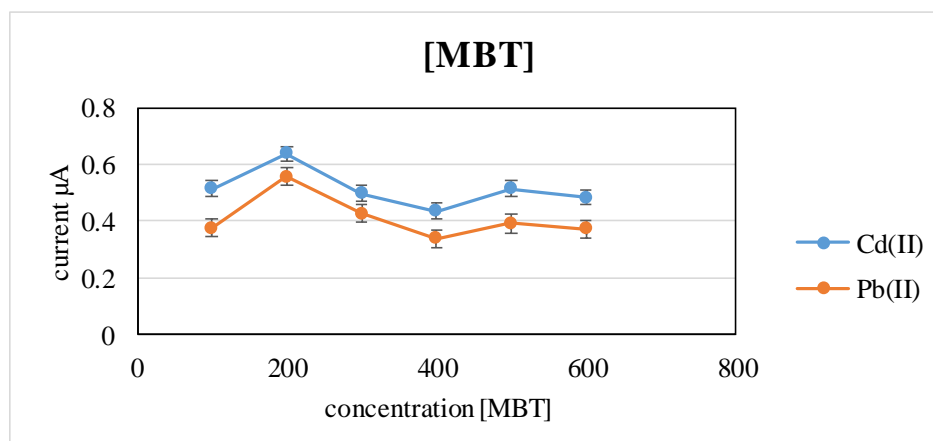
As shown in Fig 3-8, similar trend as Bi concentrations was obtained when mesoporous silica concentrations were experimented from 100 to 600  $\mu\text{g/L}$  and the same explanation can be applied, which reflects that too much meso, instead of increasing the sites, can result in less current due to the obstruction of mass transfer. The concentration of 300  $\mu\text{g/L}$  with the greatest current was chosen for further investigations (Yang, D *et al.*, 2014).



**Fig 3-8** Effect of mesoporous silica with SWASV of 20  $\mu\text{g/L}$  Cd(II) and Pb(II) pH 6 in 0.1 M acetate buffer.

### 3.1.4.6 Effect of 2-mercaptobenzothiazole concentration (MBT)

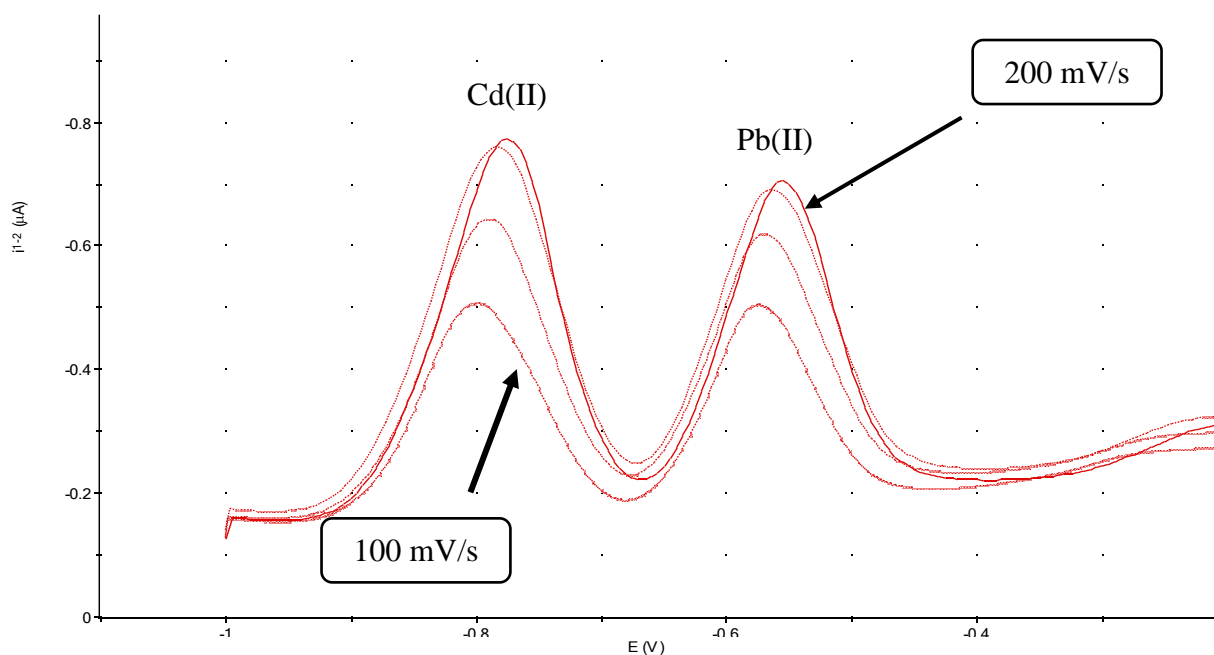
With the studied range of 100 – 600  $\mu\text{g/L}$ , the stripping current was found to be increased with MBT concentration up to 100  $\mu\text{g/L}$  and then decreased for both metals as shown in Fig 3-9. This is due to the fact that high concentration of MBT could block mass transfer of metal ions at electrode position sites. The selected MBT concentration for further experiments was therefore 200  $\mu\text{g/L}$  (Fu, X. C *et al.*, 2012).



**Fig 3-9** Effect of MBT with SWASV of 20  $\mu\text{g/L}$  Cd(II) and Pb(II) pH 6 in 0.1 M acetate buffer.

### 3.1.4.7 Effect of scan rate

The stripping scan rate was experimented from 50 to 300 mV/s. The stripping peak height was found to be increased with the scan rate from 10 to 200 mV/s as shown in Fig 3-10 and 250 mV/s is chosen for further studies with the criteria of peak shape and clarity. The concentrations used were Pb(II) and Cd(II) 0.1 mg/L, Bi(III) 0.2mg/L, MBT 0.2 mg/L, Meso 0.2 mg/L.



**Fig 3-10** Stripping peak for Cd(II) and Pb(II) which varied scan rate from 100 mV/s to 250 mV/s.

### 3.1.5 The optimum operation conditions

The parameters that affect to the analysis and optimum conditions for determination of Cd(II) and Pb(II) by Bi-Meso-MBT/GCE as a working electrode are summarized in Table 3-2.

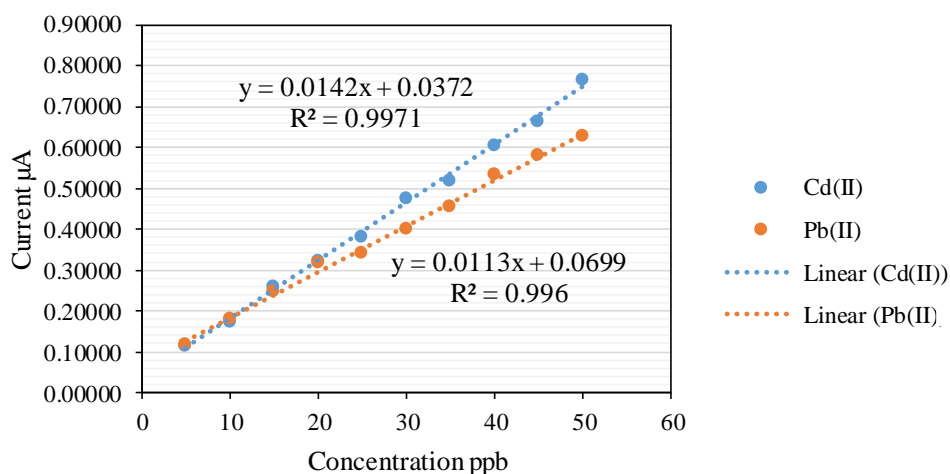
**Table 3-2** Summary of optimized operating conditions

Parameter	Studied Range	Optimum Value
Deposition potential for Pb(II) and Cd(II) detection	-1.0 V to (-1.5 V)	-1.1 V
Deposition time for Pb(II) and Cd(II) detection	100 to 500 s	300 s
Effect of pH (0.1 mol/L CH <sub>3</sub> COOH/CH <sub>3</sub> COONa)	pH 3 to 7	pH 6
Bismuth concentration	100 to 500 µg/L	200 µg/L
2-mercaptobenzothiazole concentration	100 to 600 µg/L	200 µg/L
Mesoporous silica concentration	100 to 600 µg/L	300 µg/L
Equilibration time	10 to 50 s	30 s
Step potential	1 to 20 mV	5 mV
Pulse amplitude	25 to 80 mV	75 mV
Scan rate	50 to 300 mV/s	250 mV/s

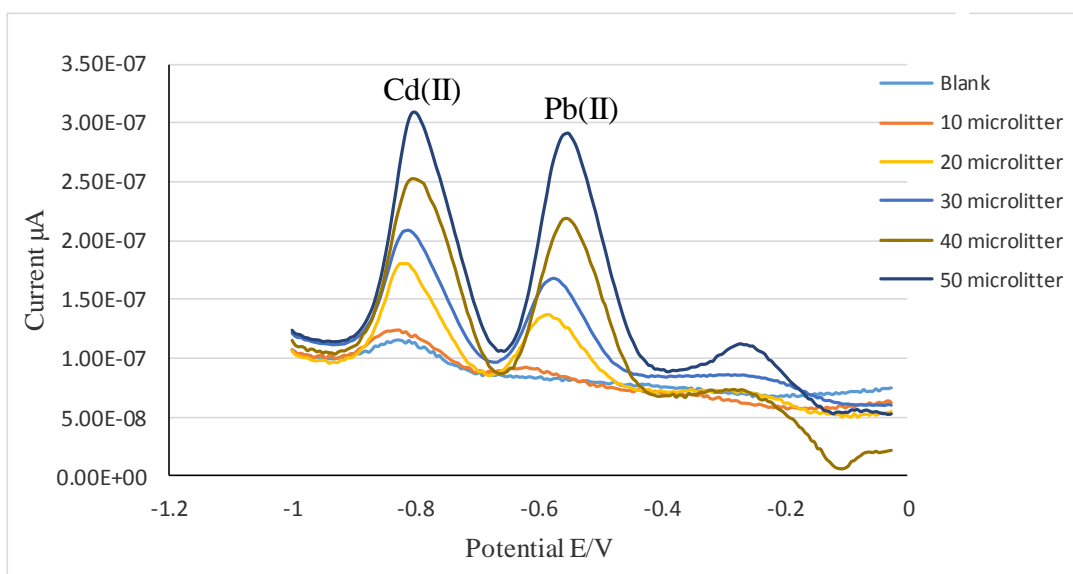
## 3.2 Analytical performance

### 3.2.1 Linear range

SWASV was used in simultaneous determination of Cd(II) and Pb(II) with the modified electrode. The linear range 5-50 ppb for both metals was obtained from calibration curves as shown in Fig 3-11. The calibration curve revealed good correlation coefficients 0.9978 for Cd(II) and 0.9960 for Pb(II). The stripping current measured at the potential of -0.845 V and -0.560 V vs Ag/AgCl for Cd(II) and Pb(II) respectively. The voltammogram are shown in Fig 3-12.



**Fig 3-11** Calibration curve for Cd(II) and Pb(II) obtained from the proposed method



**Fig 3-12** SWASV voltammograms of Cd(II) and Pb(II) in range 5 to 50 ppb

### 3.2.2 Limit of detection (LOD) and Limit of quantification (LOQ)

The limits of detections were found to be 0.56 ppb for Cd(II) and 0.80 ppb for Pb(II) by LOD of  $3\sigma/m$  where  $\sigma$  is the standard deviation from 5  $\mu\text{g/L}$  responses ( $n=10$ ) and  $m$  is the slope of the calibration curve.

The limits of quantification, LOQ, defined as  $10\sigma/m$ , were 1.87 ppb for Cd(II) and 1.66 ppb for Pb(II). The relative standard deviation was 2.97% and 2.04% for repetitive determinations ( $n=10$ ) of 20.0  $\mu\text{g/l}$  of Cd(II) and 20.0  $\mu\text{g/l}$  of Pb(II) respectively. All prove that the proposed technique was satisfactorily reproducible

and reliable for simultaneous determination of Cd(II) and Pb(II) at trace level to be applied to for real samples. The results were presented in Table 3-3.

**Table 3-3** Stripping current form 10 replications of 5 ppb Cd(II) and Pb(II) (n=10)

Replication	Current ( $\mu\text{A}$ ), $10^{-2}$	
	Cd(II)	Pb(II)
1	8.20	8.75
2	8.72	9.27
3	8.70	9.17
4	8.85	9.60
5	9.07	9.61
6	8.80	9.47
7	8.50	9.27
8	8.78	9.60
9	8.46	9.21
10	8.31	8.87
Average	0.086	0.092
SD	0.0026	0.0030
%RSD	3.072	3.248
Slop (m)	0.014	0.011
LOD ( $\mu\text{g/L}$ )	0.56	0.81
LOQ ( $\mu\text{g/L}$ )	1.87	2.67

### 3.2.3 Accuracy and Precision

The proposed method was applied to certified reference materials, natural water SRM 1640 from the National Institute of Standards and Technology (NIST), USA, to obtain satisfactory recovery of 98.02% for Cd(II) and 97.74% for Pb(II) as shown in Table 3-4.

**Table 3-4** Recovery of Cd(II) and Pb(II) in SRM 1640 water samples.

Sample	Concentration of Pb(II) and Cd(II)				%Error		%Recovery	
	Certified Value		Determination Value <sup>a</sup>		Cd(II)	Pb(II)	Cd(II)	Pb(II)
	Cd(II)	Pb(II)	Cd(II)	Pb(II)				
SRM	22.79±0.96	27.89±0.14	22.34±0.010 (%RSD = 2.97)	27.26±0.005 (%RSD = 2.04)	1.97	2.25	98.02	97.74

<sup>a</sup>Mean ± Standard deviation (n = 5)

In addition, the precision of proposed method was evaluated as %RSD of 10 replications. The %RSD of 20 ppb Cd(II) and Pb(II) determination from this method were 2.97 and 2.04% respectively. The results were shown in Table 3-5.

**Table 3-5** The current for precision measurements

Replication	Current (μA), 10 <sup>-1</sup>	
	Cd(II)	Pb(II)
1	3.35	2.51
2	3.34	2.52
3	3.57	2.62
4	3.41	2.61
5	3.49	2.59
6	3.57	2.66
7	3.44	2.57
8	3.38	2.64
9	3.56	2.62
10	3.29	2.66
Average	0.344	0.260
SD	0.0102	0.00533
%RSD	2.97	2.04

### 3.3 Interference of some coexisting ions with the determination of Cd(II) and Pb(II)

Due to the effect of the presence of other metal ions in the solution on the peak current of Cd(II) and Pb(II) were investigated. The interference study was performed by adding 1000 ppm ions into standard solution containing 20 ppb of

Cd(II) and Pb(II). Under the  $\pm 5.0\%$  tolerated ratios, It was found that Ca(II), Mg(II), Zn(II), Mn(II), Fe(II), Cu(II) and Al(III) no significant effect on the signals of Pb(II) and Cd(II) (Xiao, L *et al.*, 2014). The most interference ion with 10-fold of Cu(II) is relative bigger with more than 30% for Cd(II) and more than 20% of Pb(II) change for both metals. However, Cu(II) can be masked by using suitable and effective complexing agent such as ferrocyanide before analysis. The results were shown in Table 3-6.

**Table 3-6** Interference study of the stripping current measurements of 20  $\mu\text{g/L}$  Cd(II) and Pb(II) by the Bi-Meso-MBT/GCE in the absence and presence of interfering metal ions.

<b>Interference</b>	<b>Contribution (%) (<math>I_p</math>, Cd(II) =100%)</b>	<b>Contribution (%) (<math>I_p</math>, Pb(II) = 100%)</b>
Cu(II)	-47.17	-21.78
Zn(II)	-16.68	-13.44
Mg(II)	37.49	14.98
Ca(II)	0.48	-3.68
Al(III)	2.34	-7.63
Mn(II)	13.36	0.65
Co(II)	-4.68	-4.14
Fe(III)	5.29	7.51
Ni(II)	-4.37	-5.87

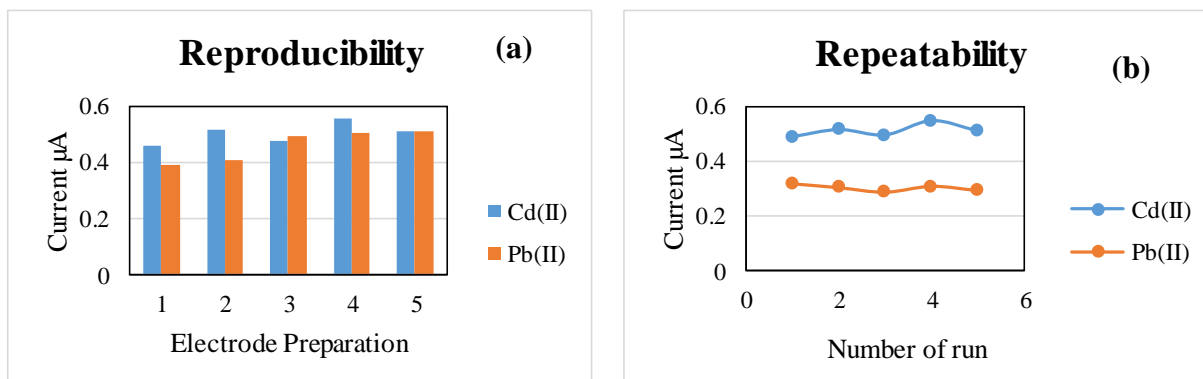
$I_p$ : peak current

### 3.4 Reproducibility and Repeatability

The reproducibility of Bi-Meso-MBT/GCE was compared by stripping current contain 20  $\mu\text{g/L}$  of Cd(II) and Pb(II) in 0.1 M acetate buffer pH 6 as shown Fig 3-13 (a). The stripping current was reproducible with good relative standard deviation (%RSD) of Cd(II) 4.45% and Pb(II) 4.06 % (Zuo, Y *et al.*, 2017). The repeatability of electrode was exhibited in 0.1 M acetate buffer pH 6 contain 20  $\mu\text{g/L}$  Cd(II) and Pb(II). The electrode was kept for 15 days as shown in Fig 3-13 (b). The result showed no significant change in the analytical response. These results of



Bi-Meso-MBT/GCE provided excellent reducibility and repeatability in stripping current of modifier under optimum conditions.



**Fig 3-13** (a) The result of reproducibility measurement of 20 ppb Cd(II) and Pb(II) with 5 preparation of electrode, (b) the repeatability with 5 times Bi-Meso-MBT/GCE when kept for 15 days measurement.

### 3.5 Method comparison

As shown in Table 3-7, the proposed method is comparable with the advantage of larger linear range, low detection limits and greater simplicity. The only disadvantage could be a little longer deposition time, which can be adjusted according to required accuracy. Other very recent methods without bismuth were also included (Entry 1-6) as references to show that our method is reasonably satisfactory.

**Table 3-7** Comparison of the proposed method for determination of Cd(II) and Pb(II) in water sample with other recent anodic stripping voltammetric methods

Entry	Electrodes	Method	Deposition time	Linear range (µg/L)		LOD (µg/L)		Ref
				Pb(II)	Cd(II)	Pb(II)	Cd(II)	
1	HMgFe-EDH/GCE	SWASV	180s	11.2 - 207	11.2 - 207	1.22	0.304	(Crowley, <i>et al.</i> , 2002)
2	ST PANI NTs	SWASV	600s	0.207 – 24.84	1.12 – 19.04	0.02	0.03	(Ma, <i>et al.</i> , 2018)
3	CA/RGO/GCE	SWASV	1500s	0.0207 – 2.07	0.112 – 13.44	0.004	0.002	(Zhu, <i>et al.</i> , 2018)
4	Nafion/CLS/PGR/GCE	DPASV	140s	10.35 - 1035	5.60 - 560	2.06	0.336	(Göde, <i>et al.</i> , 2017)
5	GO/κ-Car/L-Cys/GCE	SWASV	120s	1.03 – 10.35	0.56 – 5.60	0.12	0.12	(Yu, <i>et al.</i> , 2018)

Entry	Electrodes	Method	Deposition time	Linear range ( $\mu\text{g/L}$ )		LOD ( $\mu\text{g/L}$ )		Ref
				Pb(II)	Cd(II)	Pb(II)	Cd(II)	
6	NCQDs-GO	SWASV	300s	10.35 - 20.7	0.112 - 11200	1.16	7.4	(Priya, <i>et al.</i> , 2018)
7	In situ Bi/Graphite/Epoxy	SWASV	120s	41.4 - 352	56 - 280	14.5	5.60	(Li, <i>et al.</i> , 2018)
8	NanoSiO <sub>2</sub> -MBT/BiFE	SWASV	300s	5-50	5-50	0.80	0.56	This work

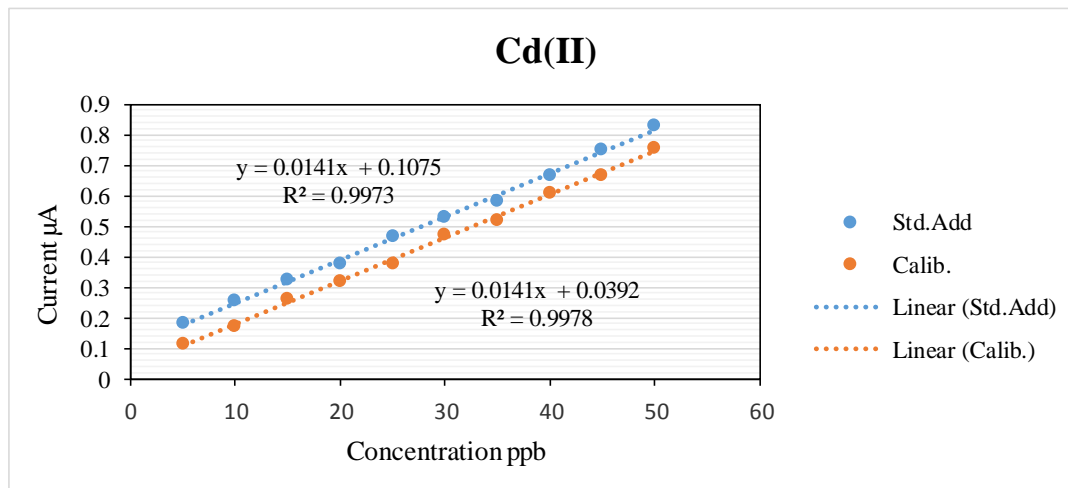
### 3.6 The comparison of the calibration and standard addition method for determination of Cd(II) and Pb(II) in tap water

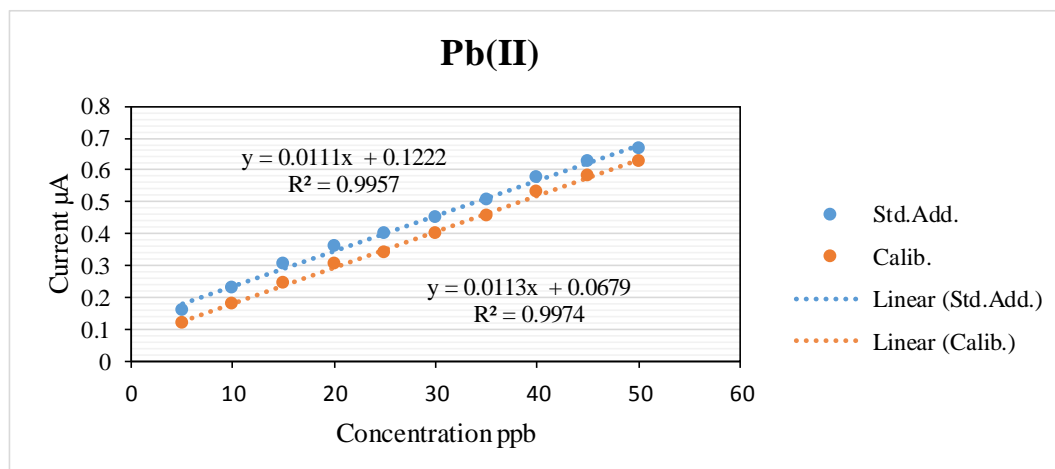
The experiment was performed by comparison between standard addition method and standard calibration curve as shown in Table 3-8.

**Table 3-8** The comparison of stripping peak current between calibration curve and standard addition method for Cd(II) and Pb(II) determination in tap water.

Cd(II) conc. (ppb)	Current ( $\mu\text{A}$ ), $10^{-1}$							
	Calibration				Standard Addition			
	Rep.1	Rep.2	Rep.3	Average	Rep.1	Rep.2	Rep.3	Average
0	0.23	0.92	1.02	0.73	1.32	1.28	1.14	1.25
5	1.15	1.23	1.02	1.13	1.55	1.20	1.28	1.34
10	1.73	1.24	1.24	1.40	2.28	1.74	1.72	1.91
15	2.61	1.60	1.50	1.90	3.08	1.32	1.77	2.06
20	3.21	2.71	2.03	2.65	3.73	2.55	3.06	3.11
25	3.79	3.51	2.01	3.10	4.51	3.07	3.55	3.71
30	4.73	3.81	2.10	3.55	5.02	3.36	3.08	3.82
35	5.20	3.95	3.09	4.08	5.86	3.73	4.15	4.58
40	6.06	5.93	4.92	5.63	6.61	4.22	4.97	5.27
45	6.65	4.50	4.01	5.05	7.00	5.98	5.59	6.19
50	7.67	6.92	5.90	6.83	8.02	6.72	6.02	6.92

Pb(II) Con. ppb	Current ( $\mu\text{A}$ ), $10^{-1}$							
	Calibration				Standard Addition			
	Rep.1	Rep.2	Rep.3	Average	Rep.1	Rep.2	Rep.3	Average
0	1.00	0.89	1.02	0.97	1.20	1.18	1.07	1.15
5	1.18	1.02	1.19	1.13	1.90	1.17	1.26	1.44
10	1.78	1.40	1.64	1.61	2.44	1.55	1.51	1.83
15	2.45	1.92	2.01	2.13	3.59	1.45	1.70	2.25
20	3.17	2.90	2.50	2.86	4.00	1.70	2.05	2.58
25	3.40	3.02	2.98	3.13	4.50	1.91	1.97	2.79
30	4.00	4.09	3.90	3.99	5.15	2.21	1.98	3.11
35	4.57	3.89	4.01	4.15	5.80	1.81	2.23	3.28
40	5.33	4.92	5.01	5.08	6.20	2.18	2.27	3.55
45	5.79	5.50	5.09	5.46	6.64	4.92	2.94	4.83
50	6.27	5.29	5.50	5.68	7.58	5.92	3.92	5.80





**Fig 3-14** Comparison of calibration curve and standard addition curve for Cd(II) and Pb(II) determination

The results from Fig 3-14 can be described that the calibration curve and standard addition curve for both Cd(II) and Pb(II) were parallel, meaning that there was no matrix interference (Abdulghani, J. A *et al.*, 2013). The slopes of standard addition and calibration curve of Cd(II) and Pb(II) were compared by t-test. The t-statistic values (Cd(II) 17.29) and Pb(II) 21.39) was more than the t-critical values (Cd(II) 2.26 and Pb(II) 2.26) value as shown in Appendix B-1. Therefore there is no significantly difference for both methods.

### 3.7 Study of percent recovery of Cd(II) and Pb(II) in tap water

To evaluate of the this method, the proposed electrode was used to examine the concentration of Cd(II) and Pb(II) in tap water samples by standard addition method. Three samples taken from different places in Hat Yai City were analyzed. As shown Table 3-9, the %recovery of Cd(II) were 100.7 – 101.3 and Pb(II) were 100.7 – 101.2. The Bi-Meso-MBT/GCE can be utilized as a selective and precision electrode to determine metal ions.

**Table 3-9** %Recovery test for the studied method using tap water sample 1<sup>st</sup>, 5<sup>th</sup>, 6<sup>th</sup> regions (n=3) spike with 5, 10, 20 and 30 ppb of Cd(II) and Pb(II)

Sample	Spike (µg/L)	Expected (µg/L)		Measured (µg/L)		%Recovery	
		Cd(II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)
Tap water 1 <sup>st</sup> region	0	-	-	ND	ND	-	-
	5	-	-	5.15±0.07	5.19±0.067	-	-
	10	10.15	10.19	10.23±0.002	10.25±0.008	100.8	100.6
	20	20.15	20.19	20.31±0.015	20.27±0.011	100.8	100.4
	30	30.19	30.19	30.35±0.011	30.36±0.015	100.4	100.5
Tap water 5 <sup>th</sup> region	0	-	-	ND	ND	-	-
	5	-	-	5.11±0.003	5.12±0.005	-	-
	10	10.11	10.12	10.19±0.01	10.20±0.007	100.8	100.8
	20	20.11	20.12	20.40±0.012	20.35±0.010	101.4	101.1
	30	30.11	30.12	30.50±0.022	30.47±0.016	101.3	101.2
Tap water 6 <sup>th</sup> region	0	-	-	ND	ND	-	-
	5	-	-	5.16±0.004	5.15±0.006	-	-
	10	10.16	10.15	10.23±0.006	10.22±0.01	100.7	100.7
	20	20.16	20.15	20.36±0.012	20.33±0.01	101	100.9
	30	30.16	30.15	30.5±0.012	30.40±0.01	101.1	100.8

Mean ± S.D (n=3), ND = None Detected

### 3.8. Application of the proposed method to tap water samples

#### 3.8.1. Determination of Cd(II) and Pb(II) in tap water sample using the studied method (ASV)

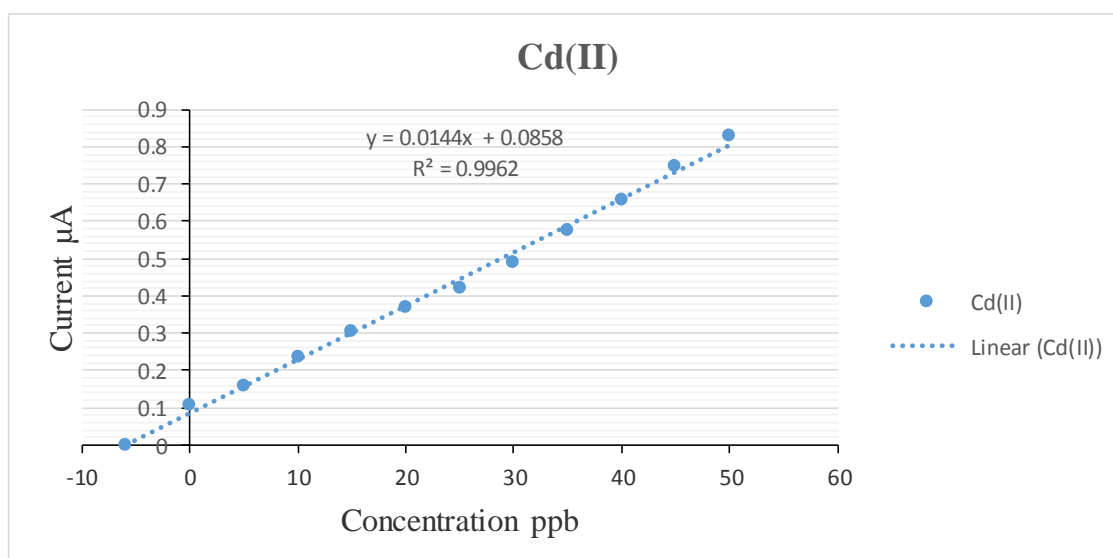
The currents from SWASV voltammogram for Cd(II) and Pb(II) determination in tap water sample from 1<sup>st</sup> region at Hat Yai City are shown in Table 3-10 and standard addition calibration curves of Cd(II) and Pb(II) in tap water samples are shown in Fig 3-15. The standard addition curve was provided good linear range 0.9962 of Cd(II) and 0.9930 of Pb(II) which is good for analyze Cd(II) and Pb(II) in real samples.

**Table 3-10** Results from standard addition for Cd(II) and Pb(II) determination in tap water sample from 1<sup>st</sup> region

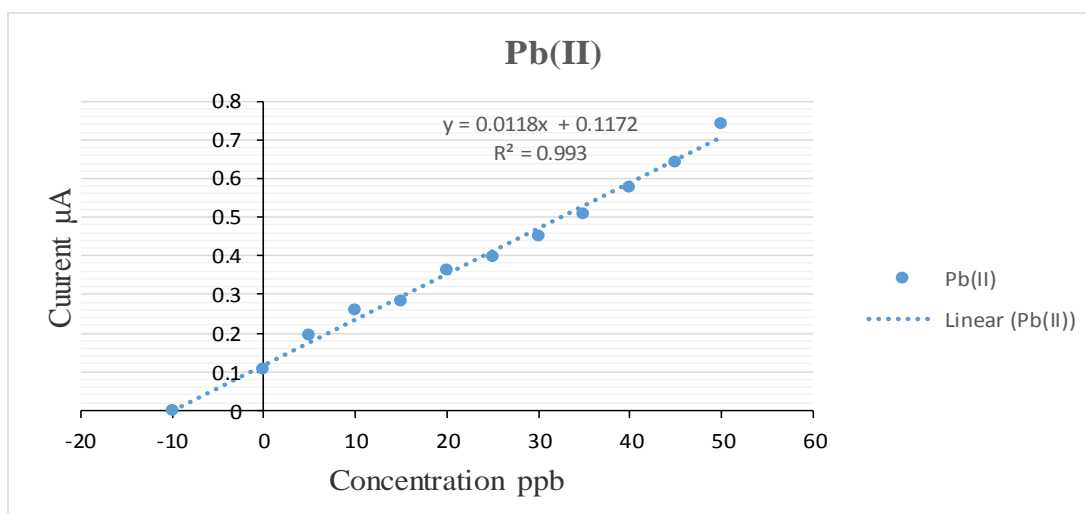
Pb(II) and Cd(II) conc. (ppb)	Current ( $\mu\text{A}$ ), $10^{-1}$	
	Cd(II)	Pb(II)
0 ppb	1.07	1.05
	1.09	1.05
	1.04	1.01
Average = Mean	0.10	0.10
Standard Deviation	0.002	0.0024
%RSD	2.40	2.39
5 ppb	1.59	1.95
	1.46	1.84
	1.56	1.96
Average = Mean	0.15	0.19
Standard Deviation	0.006	0.006
%RSD	4.46	3.53
10 ppb	2.34	2.59
	2.37	2.63
	2.37	2.48
Average = Mean	0.23	0.25
Standard Deviation	0.002	0.007
%RSD	0.86	3.05
15 ppb	3.04	2.82
	2.99	2.79
	3.27	2.61
Average = Mean	0.31	0.27
Standard Deviation	0.01	0.01
%RSD	4.88	4.04
20 ppb	3.67	3.61
	3.55	3.81
	3.46	3.51

Pb(II) and Cd(II) conc. (ppb)	Current ( $\mu\text{A}$ ), $10^{-1}$	
	Cd(II)	Pb(II)
Average = Mean	0.35	0.36
Standard Deviation	0.01	0.01
%RSD	3.03	4.22
25 ppb	4.22	3.96
	4.66	3.69
	4.72	3.66
Average = Mean	0.45	0.37
Standard Deviation	0.02	0.01
%RSD	5.92	4.46
30 ppb	4.91	4.49
	4.87	4.73
	4.99	4.78
Average = Mean	0.49	0.46
Standard Deviation	0.006	0.01
%RSD	1.21	3.25
35 ppb	5.73	5.79
	5.34	5.54
	5.55	5.63
Average = Mean	0.55	0.56
Standard Deviation	0.01	0.01
%RSD	3.57	2.27
40 ppb	6.57	5.78
	6.83	5.83
	6.95	6.01
Average = Mean	0.67	0.58
Standard Deviation	0.01	0.01
%RSD	2.84	2.11
45 ppb	7.49	6.42
	7.76	6.15

	7.85	6.06
Average = Mean	0.77	0.62
Standard Deviation	0.018	0.018
%RSD	2.39	3.04
50 ppb	8.30	7.41
	8.56	7.76
	8.86	7.78
Average = Mean	0.85	0.76
Standard Deviation	0.028	0.020
%RSD	3.27	2.68







**Fig 3-15** Standard addition curve for Cd(II) and Pb(II) in tap water sample from 1<sup>st</sup> region, concentration range from 5 µg/L to 50 µg/L

The result of Cd(II) and Pb(II) determination in tap water sample from eleven regions at Hat Yai city are shown in Table 3-11. The results suggest that the concentration of Cd(II) and Pb(II) in tap water is at trace level.

**Table 3-11** The concentration of Cd(II) and Pb(II) in tap water sample from eleven regions at Hat Yai city.

Regions	Cd(II), ppb	Pb(II), ppb
1	5.96	9.95
2	BDL	BDL
3	BDL	BDL
4	BDL	BDL
5	BDL	BDL
6	BDL	BDL
7	BDL	BDL
8	BDL	BDL
9	7.62	11.00
10	BDL	BDL
11	BDL	BDL

BDL = Below Detection Limit

### 3.8.2. Comparison between ICP-OES for Cd(II) and Pb(II) determination in tap water sample

The result from the proposed method was compared with Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) as shown in Table 3-12. The concentration of the samples assessed by ICP-OES was not showing any result as it measures below the detection limit of the instrument (0.001 ppm for Cd(II) and 0.008 ppm (Pb(II)). Meanwhile, the ASV method showed better sensitivity as it measured the concentrations of Cd(II) in region 1 and 9 of 5.96 ppb and 7.62 ppb, while the concentration of Pb(II) in the same regions are 9.95 ppb and 11.00 ppb, respectively. This result showed that the proposed method can be applied very well in real samples.

**Table 3-12** The concentration of Cd(II) and Pb(II) in tap water sample determination by ASV and ICP-OES

Regions	Cd(II) and Pb(II) concentration ppb			
	ASV		ICP-OES	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
1	5.96	9.95	BDL	BDL
2	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL
4	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	BDL
6	BDL	BDL	BDL	BDL
7	BDL	BDL	BDL	BDL
8	BDL	BDL	BDL	BDL
9	7.62	11.00	BDL	BDL
10	BDL	BDL	BDL	BDL
11	BDL	BDL	BDL	BDL
Mean	6.79	10.47	-	-

**BDL = Below Detection Limit**

## CHAPTER 4

### CONCLUSION

Cadmium and Lead in environmental can affect to human even at low concentration. Determining trace level of heavy metal ions has become very important.

In this research bismuth, mesoporous silica and 2-mercaptobenzothiazole (MBT) was modified by glassy carbon electrode to determine Cd(II) and Pb(II) in tap water sample. Metal ions accumulated on the surface of electrode were stripped off by square wave anodic stripping voltammetry (SWASV). The conditions of operation have been optimized.

Under the optimum condition, the linear correlation coefficient ( $R^2$ ) of 0.997 for Cd(II) and 0.996 for Pb(II) after 300s deposition time and deposition potential -1.1 V. The limit of detection (LOD) were Cd(II) 0.56  $\mu\text{g/L}$ , Pb(II) 0.8  $\mu\text{g/L}$  and limit of quantification (LOQ) were Cd(II) 1.87, Pb(II) 2.7 from calibration curve. Relative standard deviations (%RSD) of 20  $\mu\text{g/L}$  of Cd(II) and Pb(II) determine from this method were 2.97 and 2.04% respective. The effect of interference ions caused by cations commonly found in tap water sample especially Cu(II), Zn(II), Mg(II), Ca(II), Al(III), Mn(II), Co(II), Fe(III), Ni(II) level were investigated. Cu(II) affect the analysis significantly. It can be masked by using suitable and effective complexing agents such as ferrocyanide before analysis.

The modified electrode was applied to determine of Cd(II) and Pb(II) in tap water sample taken from eleven sites in Hat Yai city. The developed method has accuracy for determination of those metals about Cd(II) 100.7% and Pb(II) 100.8%. The concentration of Cd(II) and Pb(II) in various tap water samples were found from 0.00 to 0.00762 mg/L and 0.00 to 0.011 mg/L respectively, with standard addition method. However, the concentrations of Cd(II) and Pb(II) in water samples were lower than the permissible limits in edible portion of water (USEPA 0.015 mg/L for Cd(II) and 0.005 mg/L for Pb(II)) issues by the World Health Organization (WHO). Therefore, the Cd(II) and Pb(II) concentration in tap water samples under the investigation is safe. The method can be used satisfactorily in the analysis of tap water in local areas.

The results were in good agreement with the reference values obtained by ICP-OES method, showing acceptable practical use of the method.

All of the aforementioned prove that Bi-Meso-MBT/GCE can be a suitable method of choice in the determination of Cd(II) and Pb(II) in tap water samples.

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## APPENDIX A

### OPTIMIZATION OF THE MEASUREMENT PARAMETER

**Appendix A-1** Effect of deposition potential on 20  $\mu\text{g/L}$  Cd(II) and Pb(II) (n = 3)

Deposition Potential (V)	Peak height ( $\mu\text{A}$ ), $10^{-1}$		%RSD	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
-1	5.59	4.46	3.943	5.233
-1.1	7.17	5.41	2.581	4.774
-1.2	7.01	5.16	3.633	5.351
-1.3	7.07	5.24	3.94	4.373
-1.4	6.82	4.89	5.486	5.319
-1.5	5.34	4.08	1.957	5.759

**Appendix A-2** Effect of deposition time on 20  $\mu\text{g/L}$  Cd(II) and Pb(II) (n = 3)

Deposition time	Peak height ( $\mu\text{A}$ ), $10^{-1}$		%RSD	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
100	4.51	3.36	4.498	5.836
200	5.67	3.90	3.653	4.357
300	8.60	5.55	2.091	3.067
400	7.23	4.83	4.691	3.96
500	9.14	5.96	5.291	3.445

**Appendix A-3** Effect of pH on 20  $\mu\text{g/L}$  Cd(II) and Pb(II) (n = 3)

pH	Peak height ( $\mu\text{A}$ ), $10^{-1}$		%RSD	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
3	2.34	2.40	4.239	3.592
4	3.34	3.47	3.798	1.672
5	3.90	4.30	3.47	3.173
6	5.84	6.17	3.892	2.195
7	3.79	3.95	3.76	4.385

**Appendix A-4** Effect of Bi(III) on 20 µg/L Cd(II) and Pb(II) (n = 3)

[Bi <sup>3+</sup> ] ppb	Peak height (µA), 10 <sup>-1</sup>		%RSD	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
100	4.25	5.05	4.377	1.582
200	6.50	5.18	3.33	2.842
300	4.83	4.26	2.614	2.56
400	5.23	4.87	3.379	3.561
500	4.46	3.72	1.937	1.945

**Appendix A-5** Effect of Mesoporous Silica on 20 µg/L Cd(II) and Pb(II) (n = 3)

[Meso] ppb	Peak height (µA), 10 <sup>-1</sup>		%RSD	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
100	3.00	3.00	4.796	2.202
200	4.58	5.75	3.2181	3.544
300	2.92	3.76	2.124	2.959
400	2.69	3.57	5.804	3.574
500	2.93	3.91	1.864	4.7628

**Appendix A-6** Effect of MBT on 20 µg/L Cd(II) and Pb(II) (n = 3)

[MBT] ppb	Peak height (µA), 10 <sup>-1</sup>		%RSD	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
50	5.14	3.75	2.346	2.768
100	6.37	5.56	3.011	5.238
200	4.97	4.27	0.887	2.172
300	4.35	3.38	2.01	4.349
400	5.15	3.91	2.48	3.977
500	4.83	3.71	1.789	2.741

**Appendix A-7** Repeatability with Bi-Meso-MBT/GCE 20  $\mu\text{g/L}$  Cd(II) and Pb(II)

(n=5)

<b>Number of Run</b>	<b>Peak height (<math>\mu\text{A}</math>), <math>10^{-1}</math></b>	
	<b>Cd(II)</b>	<b>Pb(II)</b>
1	4.88	3.16
2	5.14	3.02
3	4.95	2.85
4	5.47	3.07
5	5.09	2.91
Average	0.511	0.300
SD	0.022	0.012
%RSD	4.45	4.06

**APPENDIX B**  
**STATISTICAL ANALYSIS**

Appendix B-1 comparison between standard addition and calibration curve made by

T-test

**Cd(II)**

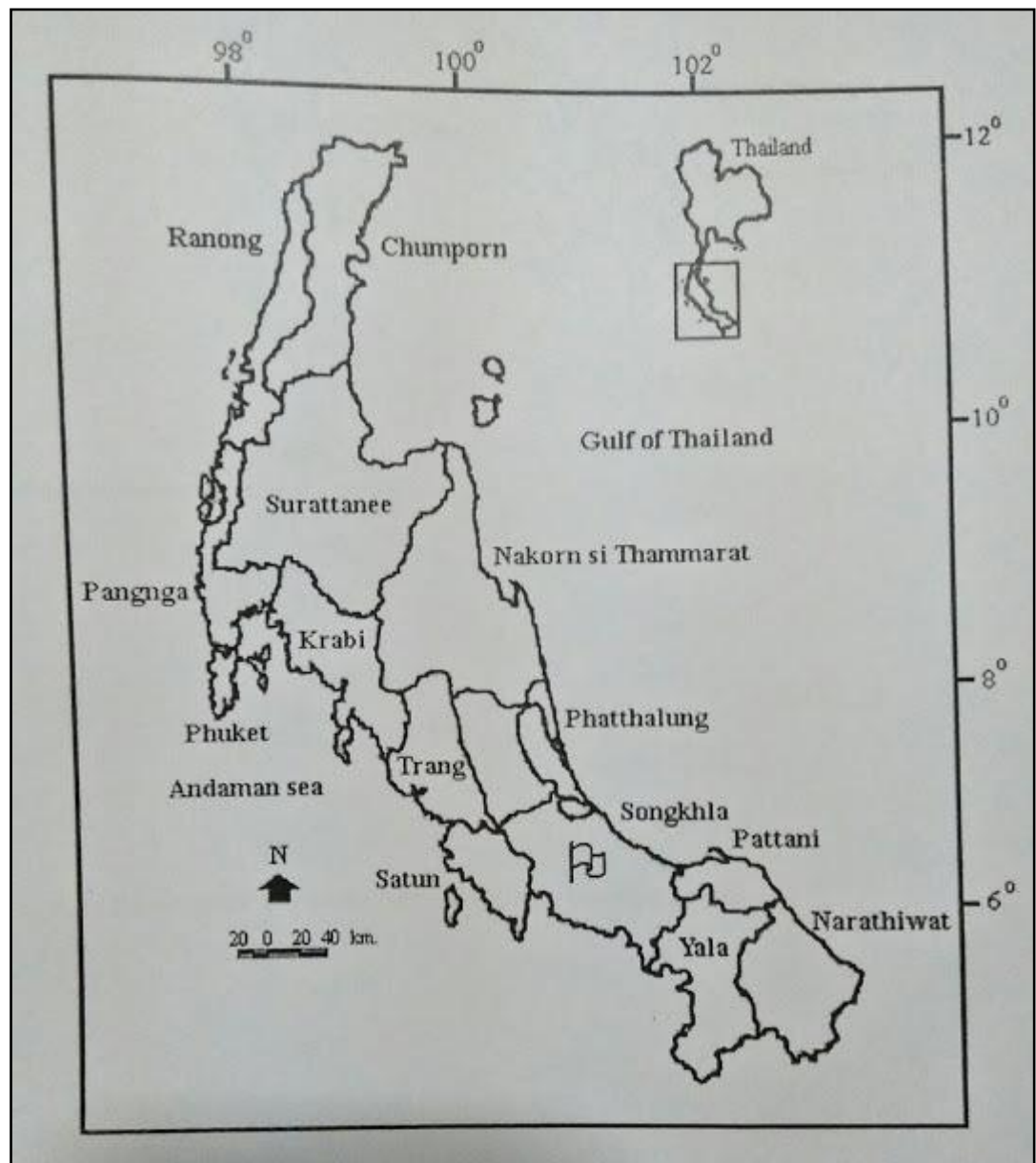
	<i>Variable 1</i>	<i>Variable 2</i>
Mean	0.496465	0.427319
Variance	0.045978378	0.045756268
Observations	10	10
Pearson Correlation	0.9982598	
Hypothesized Mean Difference	0	
df	9	
t Stat	<b>17.29163157</b>	
P(T<=t) one-tail	1.63161E-08	
t Critical one-tail	1.833112933	
P(T<=t) two-tail	3.26323E-08	
t Critical two-tail	<b>2.262157163</b>	

**Pb(II)**

	<i>Variable 1</i>	<i>Variable 2</i>
Mean	0.428654	0.378987
Variance	0.028580339	0.029408401
Observations	10	10
Pearson Correlation	0.999171512	
Hypothesized Mean Difference	0	
df	9	
t Stat	<b>21.38305655</b>	
P(T<=t) one-tail	2.51523E-09	
t Critical one-tail	1.833112933	
P(T<=t) two-tail	5.03045E-09	
t Critical two-tail	<b>2.262157163</b>	

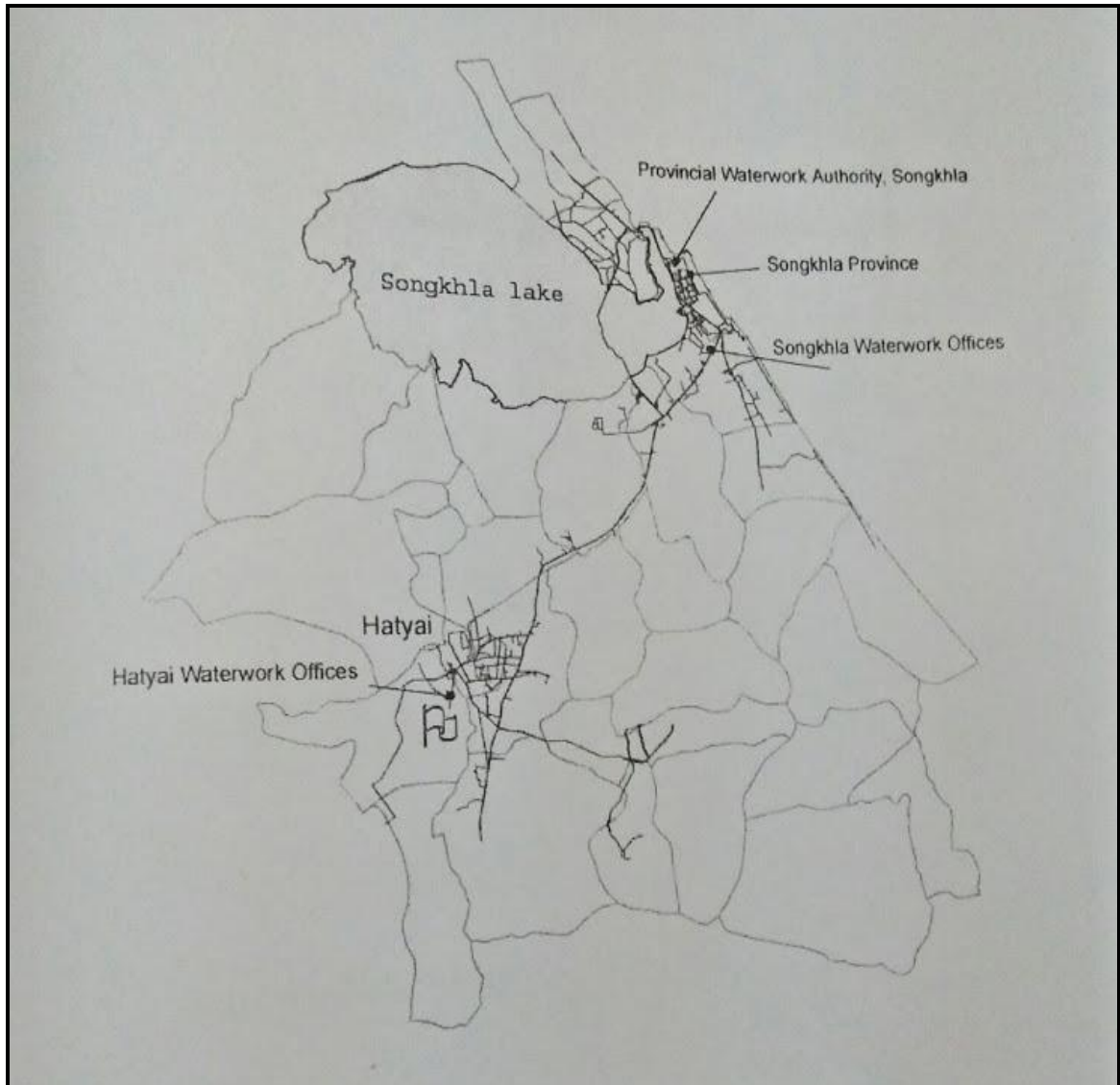
**APPENDIX C**  
**MAP OF SAMPLE COLLECTION**

**Appendix C-1** Map of tap water samples collection at Hat Yai city, in the South of Thailand, around 30 Km. From Songkhla; in February 2008 (Zoom 1<sup>st</sup> step)



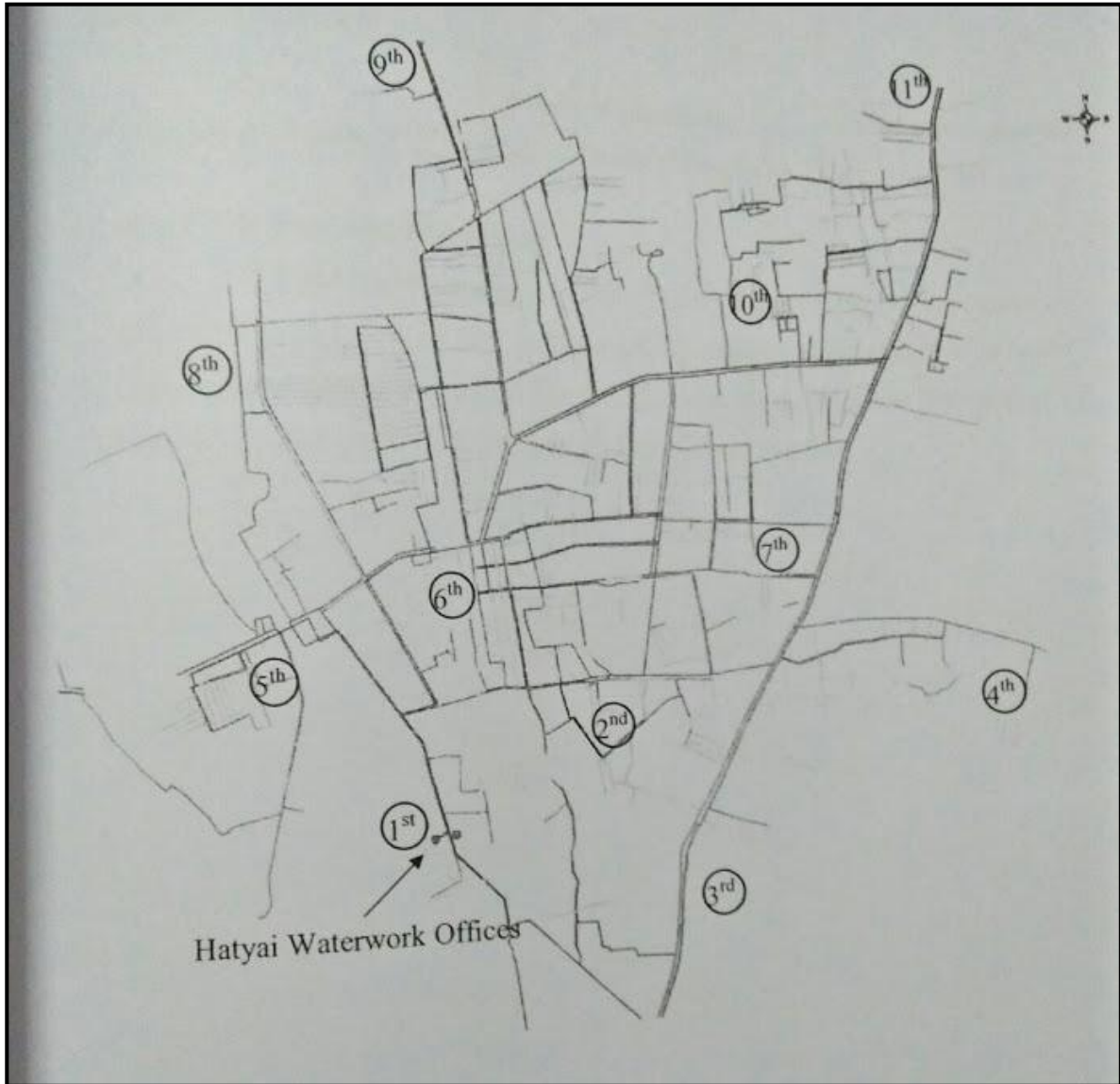
Source; [http://www.nbids.org/nbidsdata/images/S\\_map.jpg](http://www.nbids.org/nbidsdata/images/S_map.jpg)

**Appendix C-2** Map of tap water samples collection at Hat Yai city, in the South of Thailand, around 30 Km. From Songkhla; in February 2008 (Zoom 2<sup>nd</sup> step)



Source; Province Waterworks Authority (<http://www.pw.co.th>)

**Appendix C-3** Map of tap water samples collection at Hat Yai city, in the South of Thailand, around 30 Km. From Songkhla; in February 2008 (Zoom 3<sup>rd</sup> step)



Source; Hat Yai Waterworks Offices, 2007

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**List of Publication and Proceeding**

Sophy Phlay and Pipat Chooto, determination of Cd(II) and Pb(II) in tap water samples by anodic stripping voltammetry with 2-mercaptobenzothiazole modified electrode. Pure and Applied Chemistry International Conference 2018 (PACCON), the 60<sup>th</sup> Anniversary of His Majesty the King's Accession to the Throne International Convention Center, February 7-9, 2018 Hat Yai, Songkhla, Thailand.