

CHAPTER 1

INTRODUCTION

1.1 Overview of the research

The term heavy metal is often used as a group name of metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity [1]. Heavy metals such as cadmium and lead are used mainly in metal processing industries. They are found naturally in small quantities in air, water and soil. Their toxicity are well known such as cadmium seriously affects on health, causing “Itai-Itai” disease and lead interrupts physical development and nervous system.

Many techniques are employed for trace metals determination such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS) and electroanalytical techniques such as anodic stripping voltammetry (ASV). ASV can be considered as the most powerful technique for in-field analysis, due to its excellent detection limit, high sensitivity, capacity to multi element determination, high speed, simplicity and relatively low cost.

Mercury electrode has been widely used as a working electrode in ASV for several decades because it provides a wide cathodic potential limit for reduction of several metals and allows the formation of amalgams for accumulative

preconcentration of the metals leading to very high sensitivity and reproducibility for ASV determination. However, due to toxicity of the mercury [2,3], nowadays, the development of alternative materials of less toxicity and more environmentally friendly than mercury is greatly interested. Many studies have demonstrated the applicability of bismuth film electrode (BiFE) as a possible alternative for electrochemical stripping analysis of trace heavy metals, with electroanalytical behavior similar to that of mercury-based electrodes [4-6]. However, using of BiFE in batch voltammetry is tedious and not effective.

Combination of stripping voltammetry with flow system provides significant advantages over batch analysis, such as offering high level of automation, fast analysis, less risk of contamination and better reproducibility [7-14]. In this study, the flow based anodic stripping voltammetric system has been developed for determination of cadmium and lead with using of BiFE as a working electrode. The main objectives are to improve the analytical performance of ASV for determination of cadmium and lead (such as high reproducibility and sensitivity, more convenient, rapid, inexpensive and environmental friendly operation), and to apply the proposed method to the analysis of real samples.

1.2 Introduction to cadmium and lead

1.2.1 Occurrence and application of cadmium and lead

Cadmium and lead are very heavy element. They occur in nature (present in small concentrations within hardrocks) in small amounts of the Earth's crust. They are usually found in ore with zinc, silver and copper, which significant amount of them are recovered as a by-product or co-product from mining and smelting of zinc [15-16]. The cadmium and lead are removed when zinc metal is purified in a refinery process. The major forms of cadmium and lead in natural sources are sulphide form. In addition, cadmium and lead can occur as an impurity in phosphate minerals used as fertilizers [17-18].

Cadmium and lead are used mainly in metal and in a small number of other applications of processing industries such as batteries, electronics and communications, ammunition, television glass, construction, a stabilizing compound in plastics, paint pigments, protective coatings, and a wide variety of household products [19-20]. And, a small amount is used to make protective aprons for patients having x-rays to shield the body from excess radiation exposure.

1.2.2 Toxicology of cadmium and lead

Cadmium and lead are emitted from industrial and natural sources to contaminate into the environment, e.g., in air, water and soil. Heavy metals may enter the human body through food, respiratory and skin when they come in contact with humans in agriculture and in industrial, or residential settings. These metals are heavy metals that cause adverse health effects at very low exposure levels. They are well known metals seriously affect on health.

Cadmium affects many organ systems primarily. It is similar to zinc in structure and function and may replace zinc in many physiological and enzymatic functions. It is absorbed into the body in the stomach. Then spread to the liver, spleen and intestines and the cumulative increase in high doses can induces cancer and Vertebrate limb pain. It causes the kidneys impaired. Diseases caused by cadmium poisoning was called kidney disease - kidney I (Itai Itai disease)[21-22]. The degree of symptoms and severity of effects dependent on the amount of cadmium are summarized in the Table 1.1[22].

Table 1.1 Possible cadmium-induced health effects in adults[22]

Acute	Chronic
Mild/severe irritation of the upper respiratory tract, coughing, shortness of breath, pulmonary edema, pneumonitis	Kidney damage: kidney stones, proteinuria, aminoaciduria, glycosuria, renal tubular damage
GI disturbances; vomiting, abdominal pain, diarrhea, nausea, cramps	Bronchiolitis, COPD, emphysema, fibrosis
Flu-like symptoms: chills, headache, aching and/or fever	Calcium deficiency, osteoporosis, osteomalacia
	Prostate and lung cancer

Lead poisoning is one of the most common environmental health problems affecting on health. Lead can cause serious harm. When lead enters the body, it is held in the red blood cells to reduce the heme which interfere with the functioning of various enzymes, mitochondria and a neurotransmitter in the cell. It affects multiple

systems of the body such as the nervous system, kidneys, gastrointestinal tract, reproductive system and circulatory system [21]. The organ systems most sensitive to exposures of lead are illustrated in Figure 1.1[23]

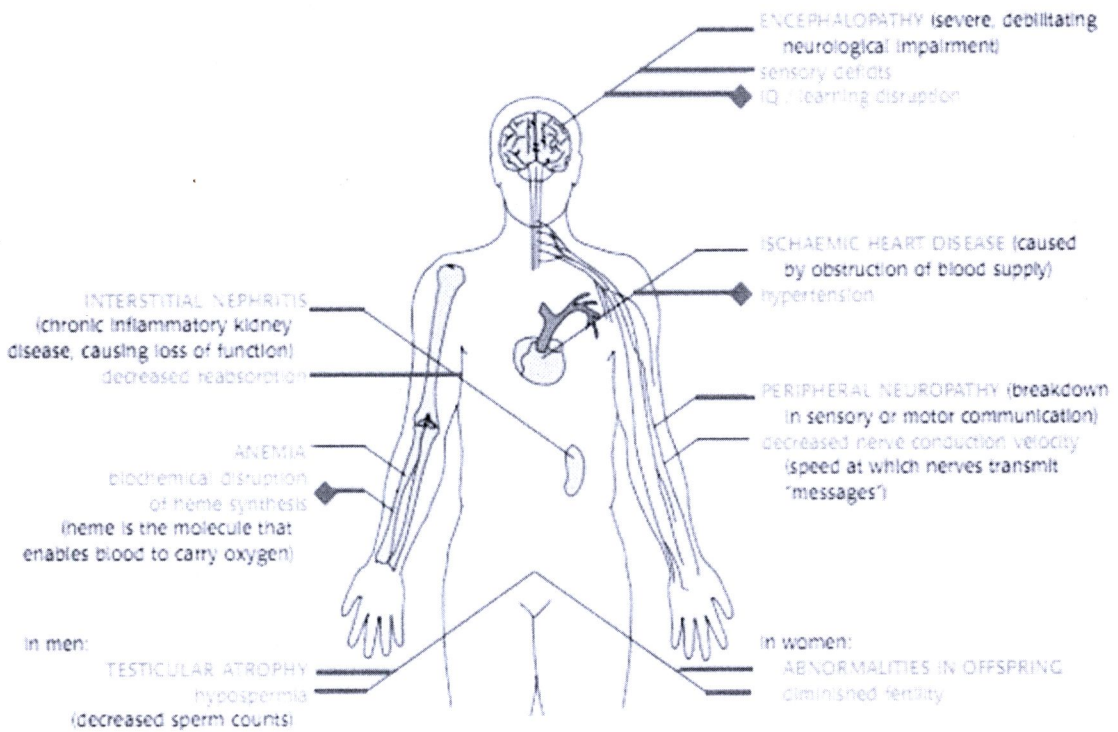


Figure 1.1 Organ systems affected by lead: — higher dose - more severe effect, — lower dose – less severe effect and ♦ Extensive study shows no evidence of "threshold" or safe exposure

1.3 Water pollution

Water is a critical factor in the maintenance of human life and also plays a role in creating stability of social but now the problem of water pollution is in the fast growing countries and more intense. There are many causes for water pollution such as contaminants that enter the water at contain the residue of human agricultural practices and improperly disposed of industrial wastes, derived from human practices (such as gaseous from automobiles), include effluent from factories, waste treatment plants[24]. The effects of water pollution with the contaminated heavy metals has damaged the food chain when humans eat the meat of the animals is infected by toxins it causes further damage to the humans and many other effects [25]. So, the Pollution Control Department regulates water quality standards from Industrial Effluent Standards of heavy metals as shown in the Table 1.2 [26].

Table 1.2 Threshold limit of heavy metals according to Thai Industrial Effluent Standards [26]

Element	Standard Values	Method for Examination
Cadmium (Cd)	not more than 0.03 mg/l	Atomic Absorption Spectrophotometry; Direct Aspiration or Plasma Emission Spectroscopy ; Inductively Coupled Plasma : ICP
Lead (Pb)	not more than 0.20 mg/l	
Chromium (Hexavalent)	not more than 0.25 mg/l	
Chromium (Trivalent)	not more than 0.75 mg/l	
Barium (Ba)	not more than 1.0 mg/l	
Nickel (Ni)	not more than 1.0 mg/l	
Copper (Cu)	not more than 2.0 mg/l	
Zinc (Zn)	not more than 5.0 mg/l	
Manganese (Mn)	not more than 5.0 mg/l	Atomic Absorption Spectrophotometry; Hydride Generation, or Plasma Emission Spectroscopy; Inductively Coupled Plasma : ICP
Arsenic (As)	not more than 0.25 mg/l	
Selenium (Se)	not more than 0.02 mg/l	
Mercury (Hg)	not more than 0.005 mg/l	Atomic Absorption Cold Vapour Technique

1.4 Anodic Stripping Voltammetry

1.4.1 Principle of stripping voltammetry

Anodic stripping voltammetry is an electrochemical method, which current is measured while voltage is applied to an electrochemical cell containing (1) electroactive analyte(s), (2) a supporting electrolyte solution, (3) a reference electrode (RE), (4) an indicator or working electrode (WE) and (5) an auxiliary electrode (AE) [27] (Figure 1.2). A current vs. voltage curve is so called a voltammogram.

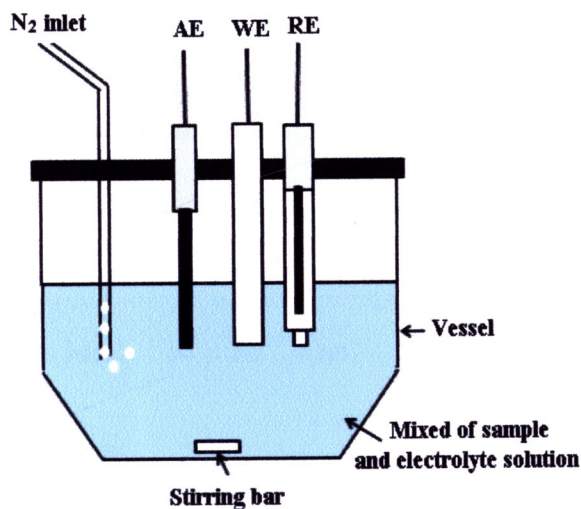


Figure 1.2 Diagram of an electrochemical cell for a voltammetric system

The diffusion current (i_d) produced by the desired reaction is proportional to the concentration of analyte (C_A) under ideal conditions,

$$i_d = k \cdot C_A \quad (1.1)$$

where k is a constant[28]. Thus, the plot of i_d versus concentration can be used for calibration.

The technique consists of two steps of operation (Figure 1.3). The first step is a preconcentration or deposition step, metal ions are deposited onto an electrode which is held at a suitable potential by reduction at the surface of WE electrode. The solution is stirred during this step to maximize the amount of metal deposited. The period of preconcentration is the so called deposition time, t_d .



The second step is stripping step, the deposited metal are stripped or oxidized from the electrode by scanning the potential toward the anodic (positive) direction. The ASV method is applied for cation determination. The current measured during the stripping step can be related to the amount of the metal in the solution [27].

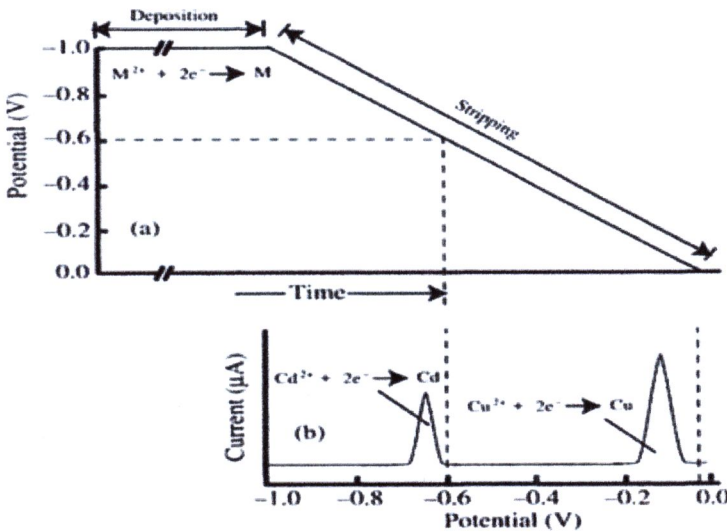


Figure 1.3 Operating step in anodic stripping voltammetric (ASV) method[27].

Since the ASV is a sensitive electroanalytical technique. It can in-situ preconcentrate trace metal ions, the detection limit of this technique is very low, i.e., ppb levels [28-29]. It can be used for the analysis of various metal ions simultaneously. This method can do quantitative and qualitative analysis.

1.4.2 Working electrodes

The working electrode is an important component of the ASV. The analyte is reduced or oxidized here. There are several electrodes which can be used as a working electrode such as mercury, glassy carbon, gold and platinum, etc.

Mercury such as Hanging Drop Mercury Electrode (HDME) is commonly used as an electrode material because it is chemically inert in most aqueous solutions and hydrogen is evolved only at very negative potentials and the wide redox working range [30-33] (Figure 1.4). It is useful because amalgams are formed with the mercury by the metals produced when the cations are reduced. Mercury electrode is a perfect electrode for ASV.

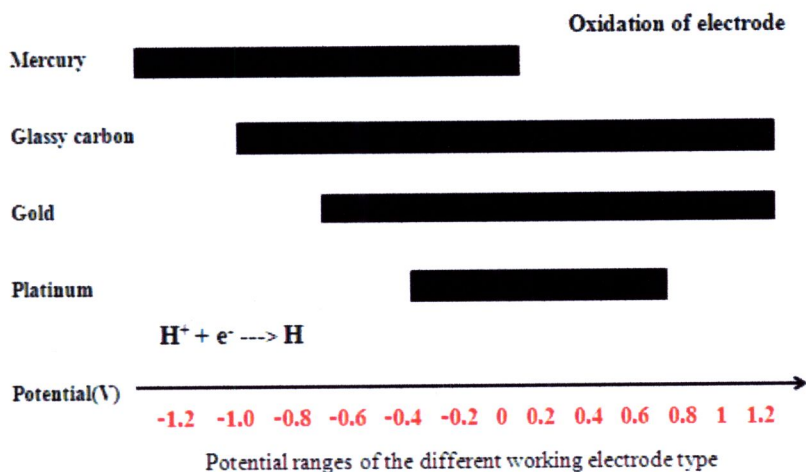


Figure 1.4 Potential ranges of the different working electrodes

1.4.3 Bismuth Film Working Electrode

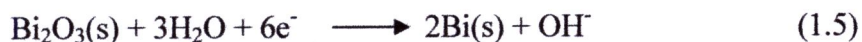
Bismuth film electrode (BiFE) is a new electrode for voltammetric analysis. It composes of metallic bismuth on a conductive supporting substrate similar to that of the conventional mercury film electrode that are being used commonly for anodic stripping voltammetric analysis [4-6, 9-14, 34-38]. However, bismuth is negligible toxic comparing to the mercury. The high sensitivity of the electrode is due to the property of bismuth to form fused alloys with heavy metals, which is analogous to the amalgams that mercury forms according to equation (1.4). Bismuth can be fusible alloys with numerous heavy metals, including lead, cadmium, thallium, antimony, indium, gallium, etc. It has been deposited on several materials, such as glassy carbon, carbon paste, screen-printed carbon ink, carbon- fibers and gold.



The advantages of this electrode are simplicity of preparation, high sensitivity, good mechanical stability, well defined and highly reproducible stripping signal, good resolution between neighboring peak, low background characteristic, less affected by potential interferences, not required deoxygenation step and more environmentally friendly. There are three methods of coating the electrode substrate with bismuth to produce a BiFE as listed below [36-38].

1. Bi_2O_3 modified electrode. In this method, the electrode is prepared by modifying the substrate electrode with Bi_2O_3 , prepared by mixing it in carbon paste to integrate it into the electrode surface. Bi_2O_3 reduces to metallic bismuth that the forms

a deposit on surface of the electrode by applying a sufficiently high negative potential [38-41] according to the reaction (1.5).



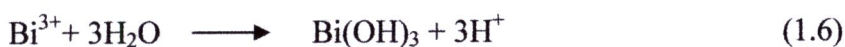
However, this method exhibits some problems in anodic stripping voltammetric analysis of metal ions such as low linearity and shift in the stripping peak potentials. Bi_2O_3 modified electrode is used for sensors because it is easy to prepare, several electrodes can be produced at the same time, and simplicity of the experimental procedure.

2. Preplating or ex situ plating bismuth electrode. This method involves electroplating of the substrate material with the bismuth from a solution containing Bi(III) ion separately, yielding a BiFE. Then, taking the electrode to the sample solution for analysis in solution or in flow system. A concentration of Bi(III) about 5-200 mg/L with a deposition potential in the negative potential and a deposition time about 1-8 min under condition of force convection (stirring or electrode rotation). The ex situ deposition of bismuth film was also proved to be a better option of film electrode preparation in case of the study of metal complexation where the presence of Bi(III) -ions in the solution could interfere with the speciation of other metals [38, 42-44].

3. In situ plating BiFE. Bi film electrode can be electrochemically formed by in situ plating, by adding Bi(III) ions directly into the sample solution and the bismuth



film is deposited together with other metals on the electrode surface during the analysis. Generally, the Bi(III) concentration must be at least 10-fold higher than the expected analyte concentration to avoid saturation effects. In situ plating method has some limitations in the accessible pH range of the sample solution. Bi(III) ions are very susceptible to hydrolysis in neutral and alkaline media according to the reaction (1.6).

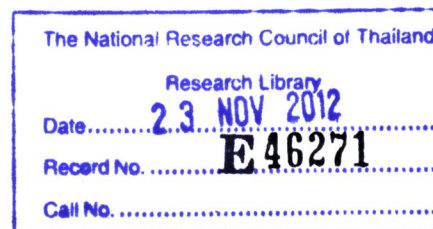


In situ plating does not require separate bismuth plating solution, this method of coating the electrode substrate is simple and shortens the experimental procedure [36, 38, 45-46]. In this work, the preparation of BiFE by in situ plating on glassy carbon was investigated.

However, using of BiFE in batch voltammetry is tedious and not effective. It consumes long time and large amounts of chemicals and give poor reproducibility. Flow techniques have been developed for voltammetric analysis to solve these drawbacks. In this work, the development of flow technique with anodic stripping voltammetric analysis using BiFE for on-line determination of trace metal ions was carried out.

1.4.4 Flow based anodic stripping voltammetry

ASV cooperated with flow techniques such as sequential injection analysis (SIA) and flow injection analysis (FIA) offers several advantages over batch analysis, e.g., fast and higher degrees of automation, improvement of accuracy and precision,



less risk of contamination, low consumption and increase degree of automation.

Several flow systems have been developed for automation of ASV analysis [7-14].

Table 1.3 summarizes some methods based on flow ASV with BiFE working electrode.

Table 1.3 Some methods based on flow anodic stripping voltammetry which employing BiFE as working electrode

No.	Analyte	Sample	Method	Ref.
1	Zn^{2+} , Pb^{2+} , Cd^{2+}	water sample	SIA system SWASV-with bismuth film electrode	[11]
2	Pb^{2+} , Cd^{2+} , organic compounds	-	FI system SWASV-with bismuth capillary electrode (BiCCE)	[47]
3	Pb^{2+} , Cd^{2+}	environmental samples	Online system SWASV-with sensor chip of microfabricated bismuth (Bi) working electrode	[48]
4	Pb^{2+}	Gunshot residues	FI system DPASV- with bismuth films co-deposited on a tubular carbon paste electrode	[49]
5	Pb^{2+} , Cd^{2+}	real sample	SI-MSFA system SWASV-with bismuth film electrode	[12]
6	Zn^{2+} , Pb^{2+} , Cd^{2+}	herbs	SIA system SWASV-with bismuth film on the screen-printed carbon nanotubes electrodes	[14]
7	Cd^{2+}	environmental water	SI-LOV system DPASV-with nafion coated bismuth film electrode	[13]
8	Pb^{2+}	tap water	FI system SWASV-with bismuth film electrode (BiFE) ex situ and in-situ plating	[50]

In this work, flow based anodic stripping voltammetric method will be developed for the simultaneous determination of cadmium and lead at trace level with bismuth film working electrode. Bismuth film in situ coated on glassy carbon electrode will be employed for preconcentration of the metals because it is more environmentally friendly than the mercury electrode and easy to prepare. The conditions for operating the system will be optimized.

1.5 Research objectives

The aims of this research can be summarized as follows:

1. To design and construct a flow system with voltammetric detection system for the determination of cadmium and lead.
2. To develop the procedure for preparation of bismuth film working electrode by in situ plating and apply for determination of cadmium and lead by flow based anodic stripping voltammetric system.
3. To apply the proposed method to the determination of cadmium and lead in real samples such as surface and ground water samples.