CHAPTER I

INTRODUCTION

1.1   Introduction

The presence of the toxic metals in the environment is associated with geological and anthropogenic processes. This problem is becoming one of the most harmful hazards to human health and environment due to the non-biodegradation and accumulation of toxic metals along the food chain [1]. Although analytical techniques for the metal detection, such as atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS) and inductively coupled plasma-mass spectrometry (ICP-MS), are commonly used to determine the metal levels in water samples with high sensitivity, in many cases these techniques are not available, especially in underdeveloped countries. Therefore, the method development for the determination of toxic metals is a challenge to find new methods that still give the reliability, good precision and accuracy. In addition, the other characteristics are required to the new analytical methodologies such as low-cost, low consumption of samples and reagents, high-throughput, portability of the instruments, computer-controlled system and so on. An alternative method, which is included numerous numbers of such requirements, is a sequential injection-anodic stripping voltammetry (SI-ASV).

SI-ASV is becoming a useful method for the metal detection due to the combination an automated flow-based system and a highly sensitive electrochemical detection [2]. The key modules of the SI system used in this dissertation are a syringe pump that is able to handing a volume of the solution precisely in a micro-scale level, and a multi-port selection valve that enables the system to sequentially select the various solutions and to subsequently change a flow direction towards the detection part of the SI system [3]. Although any detections are theoretical used in a SI system, in fact a low volume flow cell is required to give the narrow output peak, and the detector should have a fast response transducer that the distortion of the output signal does not occur. An electrochemical detection technique is therefore popularly used as a detector in SI system [4]. Furthermore, the ASV, which is one of

electrochemical detection, is ideally suited to the SI system for the determinations of metals, because it has a deposition step that the interesting metal ions are reduced and deposited on the surface of the working electrode before the measuring step. As mentioned above, SI system with ASV detection was interesting to use for the determinations of metals in this dissertation by using a low-cost working electrode, screen-printed carbon electrode (SPCE).

SPCE is a type of carbon electrode that is the most commonly used working electrode for electrochemical technique because it provides a wide electrochemical window (high cathodic limit and anodic limit), high sensitivity, and ability to use at room temperature [5-7]. The SPCEs used in this work were in-house fabricated by screen-printing technology allowing the mass production. In addition, SPCEs can be easily modified their surface by many kinds of modifiers such as enzymes, DNA sequences, metals and even nanomaterials, to achieve the electrode improvements and/or to be suitable for with the target analytes [8].

According to literature reviews, water is an essential resource that is being threatened by contamination of heavy metals such as chromium (Cr), lead (Pb), cadmium (Cd), arsenic (As) and mercury (Hg). Importantly, Hg and its derivatives is an extremely toxic pollutants [9-11]. In addition, people in many place of the world are in risk of being exposed to drinking water contaminated with high levels of As [12]. Hg(II) and As(III) were therefore chosen as representatives of toxic metals to be determined by SI-ASV. In addition, gold electrodes were found to be suitable for the determinations of As(III) [13-17] and Hg(II) [18-21]. Gold film was *in-situ* prepared on the SPCE surface by electrochemical deposition under the programmed SI system, and then the gold-modified SPCE (Au-SPCE) was used as the working electrode for the determinations of As(III) and Hg(II). Firstly, a method for the determination of As(III) by SI-ASV using *in-situ* Au-SPCE with a renewal of the Au-film was developed. The detail of the method development is described in Chapter III [22].

However, the renewal of Au-film can be achieved in only a small amount of Au on the SPCE surface; an incomplete removing of Au occurred when Au was modified on the SPCE in a large amount. The preparation of Au-film was overcome to keep the renewal property by using a small volume of 0.3 mL of the gold plating solution.

On the other hand, the small amount of Au on SPCE resulted in an insufficient detection of As. Due to roughness of surface area, a large volume of the gold plating solution was used for improvement of the detection limit, although the modified Au could not be removed completely. A procedure for cleaning the Au-SPCE to remove the residual As after analysis and to maintain the Au layer was investigated to achieve a long-lasting Au-SPCE that can be used several times by only one Au modification. The durability of the long-lasting Au-SPCE used for the determination of As concentration was demonstrated. Chapter IV describes the determination and speciation of As(III) and As(V) by SI-ASV using a long-lasting Au-SPCE, and the application of this method in real water samples was proposed [21].

Lastly, the SI-ASV using Au-SPCE has been used for the determination of Hg(II). Because the oxidation potential of Hg is close to the oxidation potential of Au, it was difficult to totally remove the remaining Hg on the Au-SPCE without damage to Au layer. Thus, the renewal Au-SPCE was used as the working electrode. Although it was found that the presence of chloride ion (Cl^-) affected the determination of Hg(II), the analysis in chloride-rich samples such as sea water sample and table salt sample was a challenge of the method development for the Hg(II) detection. On-line medium exchange was additionally appended in the procedure between the deposition step and the measuring step to remove Cl^-. The proposed method was achieved to determine Hg(II) concentration by SI-ASV with on-line medium exchange that was successfully applied in saline samples with good accuracy as described in Chapter V.

1.2 Research Objective

There are three targets for this research.

1. To develop the method for the determinations of As and Hg by SI system coupled with electrochemical detection using Au-SPCE.

2. To develop the long-lasting Au-SPCE to improve sensitivity and stability of the method for the determination of As by SI-ASV.

3. To apply the proposed method for the determinations of As and Hg in water samples with good accuracy and low detection limits.

1.3   Scope of Research

To achieve the research objectives, the following scope was set.

1. SPCEs were in-house fabricated on a ceramic substrate. The SPCE was *in-situ* modified with a gold layer by electrochemical deposition, and used for the determination of As(III) by SI-ASV. The critical parameters such as a potential scan rate of ASV, a concentration of the electrolyte solution, a deposition potential and a concentration of the gold plating solution were optimized. The analytical performance of this method was investigated in standard As(III) solutions.

2. The method for the determination of As(III) by SI-ASV using Au-SPCE was developed to obtain the lower detection limit. The long-lasting Au-SPCE was characterized and demonstrated the durability and stability in a long-term analysis. The presence of foreign cations and anions was investigated. If the results show that some considered ions can affect the measurement, the sample preparation was explored and then performed to eliminate the interfering ion. The long-lasting Au-SPCE used in SI-ASV was also applied for the determination of As(III) in real water samples under the optimal condition.

3. The SI-ASV using long-lasting Au-SPCE was applied for speciation between As(III) and As(V). The parameters for the measurement were re-optimized for the determination of As(V).   The application for determination and speciation of As(III) and As(V) in real water samples was demonstrated by using long-lasting Au-SPCE as the working electrode in the SI-ASV.

4. The critical parameters such as suitable electrolyte solution and parameters of square-wave voltammetry (step potential, frequency and amplitude) for the determination of Hg(II) by SI-ASV using Au-SPCE were optimized. Additional techniques such as a two-step deposition potential and on-line medium exchange were appended to determine Hg(II) in saline samples by SI-ASV.

1.4 Research Utilization

1. Obtain the alternative method for the determinations of As(III), As(V) and Hg(II) by automated flow-based system coupled with electrochemical technique using Au-SPCE.

2. Succeed in improving the sensitivity and stability of the method for the determination and speciation of As(III) and As(V) by SI-ASV using long-lasting Au-SPCE.

3. Obtain the SI-ASV method with good accuracy, high sensitivity and low cost for the determinations of As(III), As(V) and Hg(II) in real water samples.

There are six chapters in this dissertation. Chapter I is the Introduction. Chapter II gives the fundamental of electrochemical technique related to the metal detection and the principle of flow-based systems. Chapter III presents the method development for the determination of As(III) by SI-ASV using Au-SPCE. Chapter IV gives details of the long-lasting Au-SPCE used for the determination and speciation of As(III) and As(V) in real water samples. Chapter V reports the SI-ASV using *in-situ* Au-SPCE for the determination of Hg(II) in saline samples with high levels of Cl⁻ which can affect the measurement. Lastly, Chapter VI is the conclusions and future perspectives.