

CHAPTER V  
METHOD DEVELOPMENT FOR THE DETERMINATION OF MERCURY(II) BY  
SEQUENTIAL INJECTION/ANODIC STRIPPING VOLTAMMETRY USING AN  
IN-SITU GOLD-FILM SCREEN-PRINTED CARBON ELECTRODE

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## Abstract

A computer-controlled system, included a sequential injection system and an electrochemical detector, was developed for the determination of mercury(II) ion ( $\text{Hg}^{2+}$ ) concentrations. The screen-printed carbon electrode (SPCE), a well-known low-cost electrode, was modified by overlaying *in-situ* with a gold film (Au-SPCE). Square wave anodic stripping voltammetry (SWASV) using the Au-SPCE was performed with a two-step deposition potential of an initial  $-0.5$  V vs Ag/AgCl for the preparation of the gold film and then a deposition potential of  $+0.2$  V vs Ag/AgCl for the preconcentration of mercury. An on-line medium exchange method was included in the injection step to reduce the effect of chloride ions, whilst a solid phase extraction cartridge was used to remove interference for copper(II) ions. The flow pattern of the sequentially injected solutions with the synchronized two-step deposition potentials did not significantly affect the detection of  $\text{Hg}^{2+}$ . Square wave parameters of a 4 mV step potential, 150 Hz frequency and 30 mV amplitude gave an optimal  $\text{Hg}^{2+}$  detection sensitivity with a limit of detection of  $0.22 \mu\text{g L}^{-1}$  (sample volume of 0.9 mL) without any significant interference effect. This method was successfully applied to determine  $\text{Hg}^{2+}$  concentrations in real water samples, including in the chloride-rich samples of sea water and table salt, with very good accuracy (recovery in the range of 96.0–101%).

**Keywords:** sequential injection analysis; mercury determination; on-line medium exchange; screen-printed carbon electrode; square-wave anodic stripping voltammetry.



## 5.1 Introduction

Mercury (Hg) is used in lamps and several other industrial processes because it is a liquid metal at room temperature and can form amalgams with other metals [95]. Mercury and its compounds are applied in many industrial manufacturing processes, such as in the mining of gold (Au) and silver (Ag), and in the production of paper pulp, chlorine gas, caustic soda and even pharmaceuticals [96]. On the other hand, Hg is one of the most toxic elements that is released into the environment by anthropogenic processes where it flows through and accumulates within the food chain, especially in marine organisms [97]. Although often present at only low doses in these food chains, Hg can accumulate within the food chain over time reaching toxic levels and so threatens the environment and human health. Within humans, Hg can cause Minamata disease, renal failure, disorders of nervous systems, memory problems and even death [98]. Due to its high toxicity, the US Environmental Protection Agency and the World Health Organization have set a maximum threshold of Hg of  $2 \mu\text{g L}^{-1}$  in drinking water, based on an average water consumption of  $1\text{-}2 \text{ L d}^{-1}$  for adults [99, 100].

The most commonly used methods to determine the concentration of Hg in samples are spectrometric methods, such as atomic absorption spectrometry [101-106], fluorescence spectrometry [107-111], phosphorescence spectrometry [112] and inductively coupled plasma mass spectrometry [113-115]. Although these methods are well established, they involve time-consuming, laboratory-based techniques with large, non-mobile and expensive instruments that require trained workers to operate them. Furthermore, complicated sample preparations must be performed because the matrix contains a variety of agents that cause interference, especially, in the saline samples [107, 116]. To reduce this interference, the use of sample preparation techniques and/or sample pretreatment steps include solid phase extraction (SPE) [117] and electrochemical deposition [118].

Anodic stripping voltammetry (ASV), an electrochemical method based on the deposition of Hg on a working electrode and its subsequent stripping, is the most undertaken technique for the determination of  $\text{Hg}^{2+}$  concentration due to its sensitivity, portability and compatibility with automatic operation [22, 119]. Previous



research has shown that Au is the most suitable working electrode for the determination of  $\text{Hg}^{2+}$  levels, and has been used in the form of a Au disc or wire electrodes, a Au film on glassy carbon electrode and a Au modified screen-printed carbon electrode (Au-SPCE) [19-21, 113]. Although ASV using a Au electrode provides a high sensitivity with limits of detection (LOD) of  $\text{Hg}^{2+}$  levels in the nanomolar-scale, chloride ions ( $\text{Cl}^-$ ) in the sample matrix are an interference in the determination of the  $\text{Hg}^{2+}$  concentration because  $\text{Cl}^-$  effect the sensitivity and characteristics of the anodic stripping peak of Hg [18, 120]. A medium exchange technique for eliminating the matrix effect encountered in deposition of the sample solution has been developed in a conventional electrochemical cell and a subsequent on-line system [121, 122].

In this work, an automated system based upon sequential injection and coupled with ASV using an *in-situ* Au-SPCE for the determination of  $\text{Hg}^{2+}$  concentrations was developed. The system gave a very good precision and reproducibility [3] and has the potential for *in-situ* metal film modification of the working electrodes [64, 89, 123]. It also protects the operator from direct contact with the samples due to the on-line flow based system. Furthermore, the on-line medium exchange to eliminate the effect of  $\text{Cl}^-$  can be performed simply with this method.

## 5.2 Experimental

### 5.2.1 Chemicals and Reagents

All reagent and standard solutions were prepared with ultrapure water (resistivity  $\geq 18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) from a Milli-Q Ultrapure Water Purification System (Millipore, USA). A 1 M nitric acid ( $\text{HNO}_3$ ) solution served as the supporting electrolyte, and was prepared by dilution of 65%  $\text{HNO}_3$  (Emsure®, Merck, Germany). A Au plating solution was accurately prepared by dilution of a  $\text{Au}^{3+}$  standard solution (standard grade for atomic absorption spectroscopy,  $1002 \text{ mg L}^{-1}$ , Fluka, Switzerland) with 1 M  $\text{HNO}_3$ . A standard  $1 \text{ mg L}^{-1}$   $\text{Hg}^{2+}$  solution (standard grade for atomic absorption spectroscopy,  $1000 \text{ mg L}^{-1}$ , Fluka, Switzerland) was diluted as required with 1 M  $\text{HNO}_3$  to obtain the final desired concentration.



### 5.2.2 Apparatus

The automated flow-based system in this work utilized a sequential injection (SI) system (Auto-Pret MP-014S, MGC Japan) that consisted of a syringe pump (PSD4, Hamilton, USA), a PTFE holding coil, an eight-port selection valve (MVP, Hamilton, USA), a six-port switching valve (although this was not used in this work), and PTFE tubing (0.75 mm i.d.). The system was controlled by computer software developed in house.

The electrochemical detection and *in-situ* Au-film preparation was performed by a potentiostat (Autolab PGSTAT30, Metrohm Autolab, The Netherlands). A thin-layer flow cell (cross-flow cell, Bioanalytical Systems, USA), used as the detection part, and consisted of a three-electrode system of the *in-situ* Au-SPCE as the working electrode, an Ag/AgCl electrode (3 M KCl) as the reference electrode and a stainless steel tube as the counter electrode as well as the outlet of the flow cell. The flow cell was housed in a Faradaic box to extenuate electrical noise.

### 5.2.3 Preparation of the SPCE

The SPCEs were prepared in house. First, silver ink (Electrodag 7019, Acheson, USA) was screen-printed onto the ceramic substrate and then baked in an oven at 55 °C for 2 h to dry the ink, and then repeated screen-printing over the same area and baking under the same conditions. The dried silver then pad served as the conducting pad of the SPCE. In the second step, carbon ink (Electrodag PF-407C, Acheson, USA) was screen-printed onto the conductive pad, baked under the same conditions and the procedure repeated one more time over the same area. Finally, the printed ceramic plate was appropriately cut and used as the working electrode.

### 5.2.4 Step Sequence

A schematic diagram of the SI/square wave ASV (SI/SWASV) used in this work is shown in Figure 5.1. The step sequence with the optimal parameters for the *in-situ* Au film preparation and the determination of  $\text{Hg}^{2+}$  concentration by SI/SWASV are shown in Table 5.1.



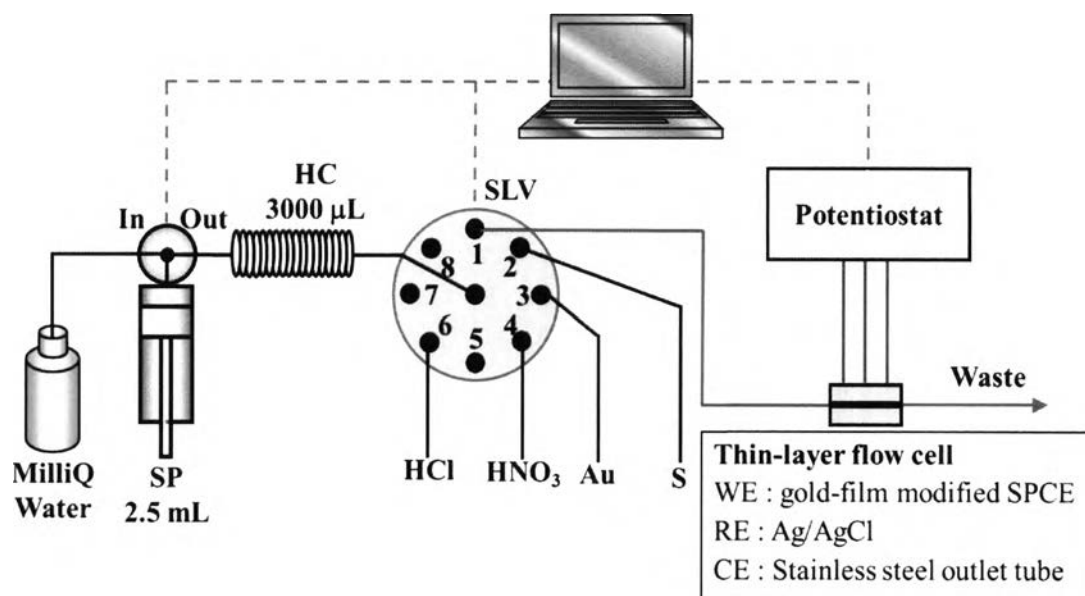
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Table 5.1 Step sequence for the *in-situ* Au film preparation and the determination of mercury by SI/SWASV.

Step	Operating Description	Selection valve position [port number]	Syringe pump status	Volume ( $\mu\text{L}$ )	Flow rate ( $\mu\text{L s}^{-1}$ )	Electrode potential (V)	Time (s)
1	Sequentially aspirate solutions into the holding coil	[4] 1 M $\text{HNO}_3$	Aspirate	200	200	-0.3 <sup>a</sup>	20
		[2] Sample	Aspirate	900	200	-0.3 <sup>a</sup>	
		[3] 500 $\mu\text{g L}^{-1}$ Au(III)	Aspirate	900	200	-0.3 <sup>a</sup>	
2	Dispense the solutions in the holding coil for <i>in-situ</i> Au film preparation and the deposition of Hg	[1] Flow cell	Dispense	2000	10	-0.5 <sup>b</sup>	90
						+0.2 <sup>c</sup>	110
3	Equilibration	-	Delay	-	-	+0.0	3
4	Stripping and recording voltammogram	-	Delay	-	-	Scan (+0.0 to +1.0)	12
5	Cleaning and conditioning the electrode for the next analysis	[6] 1 M HCl	Aspirate	2500	200	+1.2 <sup>d</sup>	100
		[1] Flow cell	Dispense	2500	100	+1.2 <sup>d</sup>	
		[4] 1 M $\text{HNO}_3$	Aspirate	2500	200	+1.2 <sup>d</sup>	
		[1] Flow cell	Dispense	2500	100	+1.2 <sup>d</sup>	
						Total time (s)	335

<sup>a</sup> Standby potential, <sup>b</sup> Deposition potential for Au, <sup>c</sup> Deposition potential for Hg, <sup>d</sup> Cleaning potential



**Figure 5.1** Schematic diagram of the SI/SWASV system used for the *in-situ* Au film preparation and the determination of  $\text{Hg}^{2+}$  concentration.

(SP, syringe pump; HC, holding coil; SLV, eight-port selection valve; S, standard/sample solution; Au,  $\text{Au}^{3+}$  plating solution;  $\text{HNO}_3$ , 1 M  $\text{HNO}_3$  solution for the electrode cleaning and displacement of the dead volume;  $\text{HCl}$ , 1 M  $\text{HCl}$  solution for the electrode cleaning; WE, working electrode; RE, reference electrode; CE, counter electrode).

The determination of the  $\text{Hg}^{2+}$  concentration was performed in five steps. First, an electrolyte solution for the stripping step (1 M  $\text{HNO}_3$  solution), the test sample solution, and an Au plating solution ( $500 \mu\text{g L}^{-1}$   $\text{Au}^{3+}$  solution in 1 M  $\text{HNO}_3$ ) were sequentially aspirated into the holding coil and the potentiostat was started at a standby potential. Next, the selection valve position was changed to the position of flow cell and the syringe pump dispensed the aspirated solutions from the holding coil in the reverse direction with aspiration. Therefore, the first solution to enter the flow cell was the Au plating solution. A  $-0.5$  V vs  $\text{Ag}/\text{AgCl}$  potential for 90 s was used for the deposition of Au, and this was followed by the entry of the test sample solutions with the potential set at  $+0.2$  V for 110 s for the deposition of Hg and then the pure electrolyte solution. The pure electrolyte solution in this step was used as a medium exchange solution as well as a displacement solution for the dead volume in the system. Therefore,  $\text{Hg}^{2+}$  in sample solution was deposited on

the electrode surface in the electrolyte solution of 1 M HNO<sub>3</sub> and then the fresh electrolyte solution was changed for the stripping step. The third step was an equilibration step in which the syringe pump stopped for 3 s. Fourthly, the measurement step was performed where the ASV was recorded from the potential of +0.0 to +1.0 V with a square-wave waveform (frequency of 150 Hz, step potential of 4 mV, and amplitude of 30 mV). Finally, the electrode was cleaned by 1 M HCl and 1 M HNO<sub>3</sub> solutions with an applied potential of +1.2 V for 100 s (step 5 in Table 5.1). The cleaning potential oxidized and removed the Au film and remaining analytes on the electrode. Therefore, the electrode was available for several analysis reuses. All experiments were performed at natural room temperature (~25-27 °C).

### 5.3 Results and Discussion

#### 5.3.1 Effect of the Supporting Electrolyte Solution

Three acid solutions, namely hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), and perchloric acid (HClO<sub>4</sub>), were evaluated at 1 M concentration as the supporting electrolyte because in general metal ions are stable in the cationic form under an acidic condition [57]. For each acid electrolyte solution, the determination of Hg<sup>2+</sup> was performed using a 50 µg L<sup>-1</sup> Hg<sup>2+</sup> by SI/SWASV. The oxidation peak of Hg<sup>2+</sup> in 1 M HCl had a lower potential compared with those from the other two supporting electrolyte solutions (Figure 5.2), which implies that the oxidation of Hg<sup>2+</sup> in 1 M HCl occurred more easily than in the two other supporting electrolytes because the chloride salt of the stripped Hg<sup>2+</sup> could be formed [18]. However, 1 M HCl was inappropriate as an electrolyte solution due to lower obtained anodic peak current, while 1 M HNO<sub>3</sub> gave the highest peak current. Because sensitivity is an important property of any quantitative method to achieve a LOD, HNO<sub>3</sub> was selected as the supporting electrolyte.





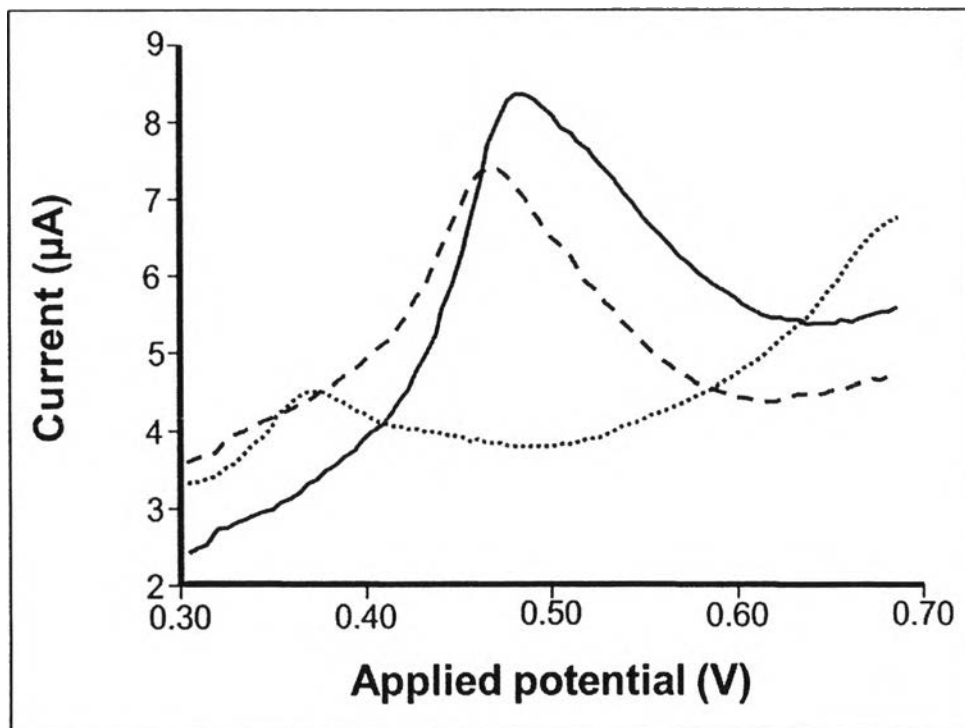


Figure 5.2 Typical square wave anodic stripping voltammograms on the *in-situ* Au-SPE of  $50 \mu\text{g L}^{-1} \text{Hg}^{2+}$  in 1 M electrolyte solutions of HCl (dotted line),  $\text{HClO}_4$  (dashed line) and  $\text{HNO}_3$  (solid line).

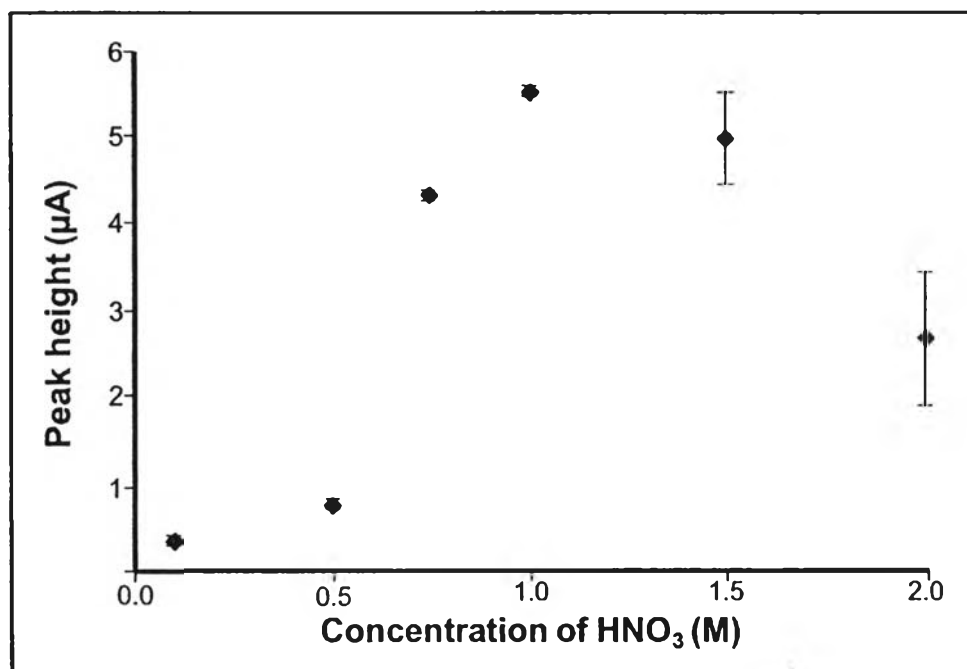


Figure 5.3 Effect of the  $\text{HNO}_3$  electrolyte concentration on the anodic stripping peak current of  $50 \mu\text{g L}^{-1} \text{Hg}^{2+}$  by SI/SWASV.

Thereafter, the concentration of  $\text{HNO}_3$  electrolyte solution was investigated over range of 0.1 M to 2.0 M (Figure 5.3). The resulting stripping peak height of  $\text{Hg}^{2+}$  increased when the concentration of the  $\text{HNO}_3$  electrolyte solution increased from 0.1 M to 1.0 M due to the increased ionic strength. However, the sensitivity and accuracy of the analysis dropped 1.1- and 2.0 fold as the  $\text{HNO}_3$  - concentration was increased to 1.5 M and 2.0 M, respectively, because the hydrogen gas generated by the electrochemical reduction covered the electrode's surface [71, 87, 124]. Accordingly, the suitable supporting electrolyte solution for this work was 1 M  $\text{HNO}_3$ .

### 5.3.2 Chloride effect and on-line medium exchange

For determining the  $\text{Hg}^{2+}$  concentration in chloride-rich samples, such as tap water, sea water and a table salt solution, the  $\text{Cl}^-$  will interfere in the analysis as seen when using 1 M HCl as electrolyte solution (Figure 5.2). In the stripping step, Au and Hg can be dissolved in a solution containing a high concentration of  $\text{Cl}^-$  without an electrochemical reaction, and the oxidation of Au then occurred at a potential of about +0.7 V vs Ag/AgCl, which a shift to a lower potential compared to the common oxidation peak potential of Au at about +0.9 V vs Ag/AgCl [57]. Moreover, it has been reported that various concentrations of  $\text{Cl}^-$  between 1 mM and 5 mM also result in the shift of peak potential [122]. Therefore, the presence of  $\text{Cl}^-$  affected the amount of deposited Hg and the stability of the Au film on the SPCE surface. To solve this problem, an on-line medium exchange procedure has been developed.

In this work, the SI system was coupled with a thin layer flow cell with a three-electrode system, which is suitable to perform an on-line medium exchange procedure. A small volume of fresh supporting electrolyte (1 M  $\text{HNO}_3$ ) was subsequently injected into the flow cell before the measurement step, which only takes 20 s. This method was used for determination of  $\text{Hg}^{2+}$  in a standard solution containing  $50 \mu\text{g L}^{-1} \text{Hg}^{2+}$  in 1 M HCl. The increase in the anodic stripping peak height of Hg was found to be 2.5-fold more than that in the absence of the medium exchange procedure (Figure 5.4). Therefore, this result supported that the on-line medium exchange procedure was effective for subsequent determination of the  $\text{Hg}^{2+}$  concentrations in chloride-rich samples.



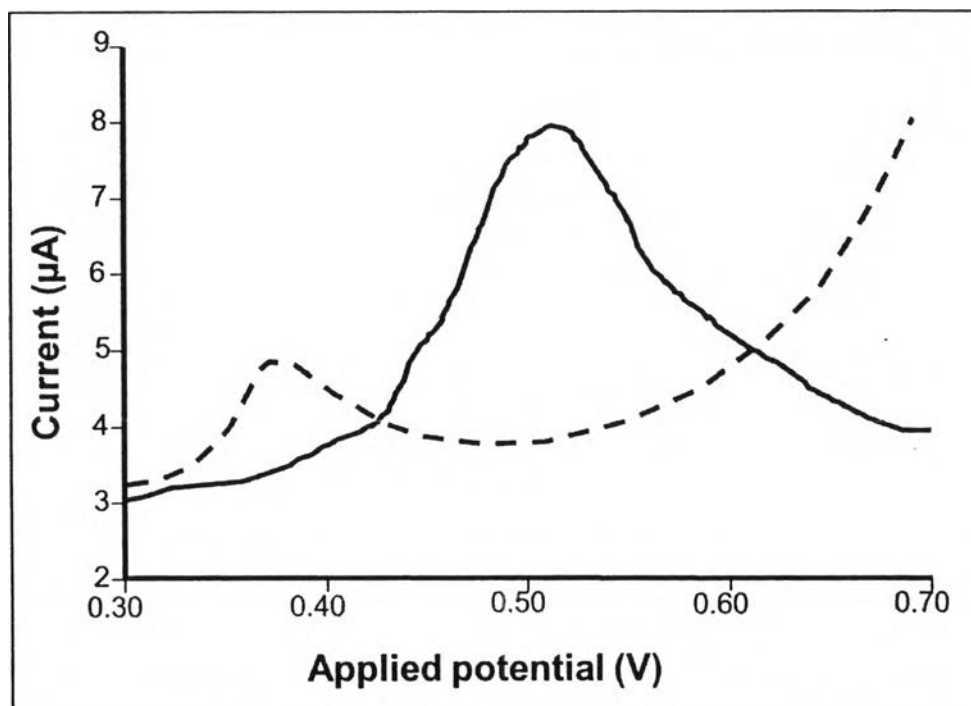


Figure 5.4 Typical square-wave anodic stripping voltammograms on the *in-situ* Au-SPCE of  $50 \mu\text{g L}^{-1} \text{Hg}^{2+}$  in 1 M HCl, either following the medium exchange method to remove  $\text{Cl}^-$  ion (solid line) or without the medium exchange method (dashed line).

### 5.3.3 Electrode Cleaning Step

The electrode cleaning solution was then optimized in order to remove the residual analytes and gold film on the electrode surface after the stripping step. From the observed effect of the presence of  $\text{Cl}^-$  on the Hg oxidation potential, 1 M HCl was also used as the cleaning solution in comparison with 1 M  $\text{HNO}_3$ . A high  $\text{Hg}^{2+}$  concentration ( $1000 \mu\text{g L}^{-1}$ ) was analyzed by SI/SWASV using either 1 M HCl or 1 M  $\text{HNO}_3$  as the cleaning solution, and then SI/SWASVs of the pure electrolyte solution (1 M  $\text{HNO}_3$ ) were performed to check the level of residual of Hg on the electrode. When 1 M  $\text{HNO}_3$  was used as the cleaning solution, an anodic stripping peak of Hg was still found, whereas the voltammograms of the supporting electrolyte when 1 M HCl was used as the cleaning solution were clean and smooth. Therefore, 1 M HCl was selected as the cleaning solution. However, the voltammograms were not clear after 10 repeated analyses, so 1 M  $\text{HNO}_3$  was additionally used to clean the

electrode after cleaning with 1 M HCl. The voltammograms of this electrode cleaning procedure were then found to be smooth in long term analysis. It is plausible that the addition of HNO<sub>3</sub> served as an aqua regia for removal of the Au film to renew the electrode surface.

#### 5.3.4 Two-step Deposition Potential and Flow Pattern of the Sequentially Injected Solutions

Using the SI system, the solutions can be injected into the flow cell sequentially, so each solution that was aspirated into the system was separated in the tubing as a flow stream. The advantage of this is that the deposition potential for the preparation of the *in-situ* Au film and that for the accumulation of Hg can be performed at different potentials. The deposition potential for the preparation of the Au film was evaluated between -0.6 V and -0.1 V using one-step deposition potential. The deposition potential for the Au film preparation that gave the highest peak current of Hg was found to be -0.5 V. Hence, the deposition potential for the accumulation of Hg was investigated between -0.5 V and +0.5 V with the fixed deposition potential of the Au film preparation of -0.5 V to find the minimum required deposition potential for Hg accumulation. The optimal deposition potential for accumulation of Hg was +0.2 V (Table 5.2). Furthermore, the concentration of the Au<sup>3+</sup> solution was evaluated from 100 to 3000 µg L<sup>-1</sup> and the best result was obtained when using 500 µg L<sup>-1</sup> Au<sup>3+</sup> for the Au film preparation.





Table 5.2 Summary of optimized experimental conditions for the determination of Hg(II) by SI/SWASV using *in-situ* Au film SPCE.

Parameters	Examined	Optimum
Type of supporting electrolyte solution	HCl, HNO <sub>3</sub> , HClO <sub>4</sub>	HNO <sub>3</sub>
Concentration of the supporting electrolyte, HNO <sub>3</sub> (M)	0.10, 0.50, 0.75, 1.0, 1.5, 2.0	1
Deposition potential for preparation of Au film (V)	-0.6, -0.5, -0.4, -0.3, -0.2, -0.1	-0.5
Deposition potential for accumulation of Hg (V)	-0.5, -0.2, +0.0, +0.1, +0.2,+0.3,+0.4, +0.5	+0.2
Concentration of Au(III) solution for preparation of Au film ( $\mu\text{g L}^{-1}$ )	100, 500, 700, 1000, 3000	500
- Square wave parameters		
- Step potential (mV)	0.5, 1, 2, 3, 4, 5	4
- Frequency (Hz)	25, 50, 100, 150	150
- Amplitude (mV)	5, 10, 20, 30, 40, 50	30

When the solutions were aspirated sequentially into the holding coil and then dispensed into the flow cell, where the deposition potential was  $-0.5$  V (for the preparation of the Au film) and then immediately changed  $+0.2$  V (for the accumulation of Hg), they could partially mix at their respective interfaces. This boundary mixing may affect the efficiency of the  $\text{Hg}^{2+}$  determination and so to evaluate this a 0, 200, 500  $\mu\text{L}$  fraction of 1 M  $\text{HNO}_3$  was added to separate the  $\text{Au}^{3+}$  solution from the sample solution (Figure 5.5). The typical square wave anodic stripping voltammograms gave a Hg anodic peak height of 2.2, 2.2 and 2.3  $\mu\text{A}$  for addition of a 0, 200, 500  $\mu\text{L}$  separating  $\text{HNO}_3$  fraction between the  $\text{Au}^{3+}$  and test samples, respectively (Figure 5.6). Thus, the mixing of solutions in the holding coil did not significantly affect the  $\text{Hg}^{2+}$  detection ability using this two-step deposition process, and so simplest method of the Au-sample sequential injection without the addition of a separating 1 M  $\text{HNO}_3$  fraction was selected.

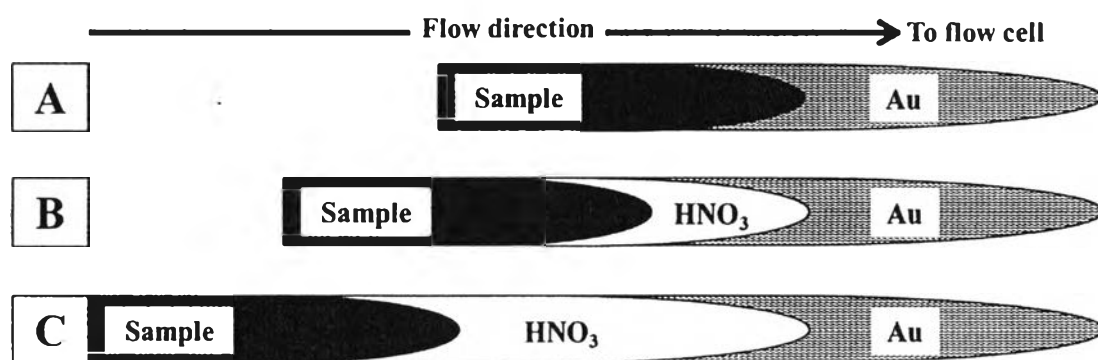


Figure 5.5 Schematic diagrams of the likely different flow pattern obtained by the three injection methods of the Au-sample with a separating 1 M  $\text{HNO}_3$  interlayer of 0 (A), 200 (B) and 500 (C)  $\mu\text{L}$ .

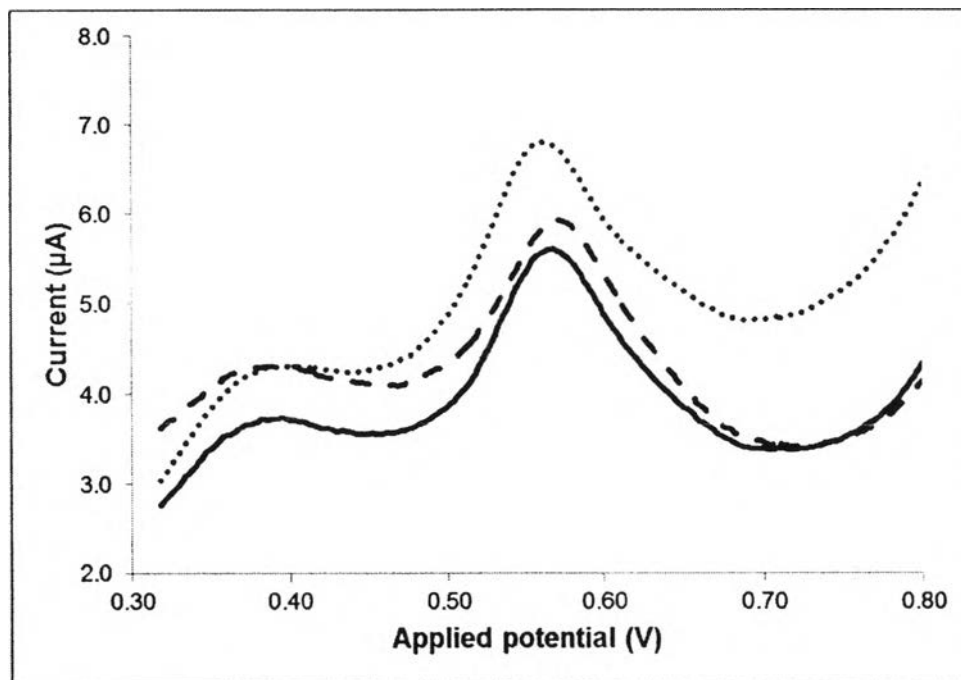


Figure 5.6 Typical square wave anodic stripping voltammograms on the *in-situ* Au-SPCE of  $20 \mu\text{g L}^{-1}$   $\text{Hg}^{2+}$  in  $1 \text{ M HNO}_3$  with a Au-sample separating  $1 \text{ M HNO}_3$  interlayer of 0 (solid line), 200 (dashed line) and 500 (dotted line)  $\mu\text{L}$ .

### 5.3.5 Analytical Characteristics

The frequency and amplitude of the square wave-wave form of the SWASV were optimized, and the results are summarized in Table 5.2. Under the optimized conditions, the calibration graph for the determination of  $\text{Hg}^{2+}$  concentrations by SI/SWASV using the *in-situ* Au-SPCE was found to display a linear relationship between the anodic stripping peak height and the concentration of  $\text{Hg}^{2+}$  in a range of  $1\text{--}20 \mu\text{g L}^{-1}$  with a calibration equation of  $y=0.1956x+0.5376$  ( $R^2=0.9994$ ). The limit of detection (LOD, the concentration corresponding to three times the standard error of the calibration graph's linear regression) was  $0.22 \mu\text{g L}^{-1}$ , whilst the repeatability was calculated from the determinations of  $\text{Hg}^{2+}$  in a standard solution containing  $20 \mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$ , had a relative standard deviation (RSD) of 6.8% which is acceptable for this concentration range according to AOAC guidelines.

### 5.3.6 Interference Study

The interference of foreign metal cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ), which are generally contained in natural water, were individually evaluated at a concentration of  $1000 \mu\text{g L}^{-1}$  in the presence of  $20 \mu\text{g L}^{-1} \text{Hg}^{2+}$  (50-fold the  $\text{Hg}^{2+}$  concentration). The anodic stripping peak of Hg was clearly overlapped with that for Cu, and the anodic stripping peak current of Hg was reduced slightly (by 0.6%) in the presence of  $\text{Pb}^{2+}$  compared to the peak current without the foreign cations. However, all the other tested cations did not have a discernible effect on the anodic stripping peak of Hg. Therefore, a lower concentration of  $100 \mu\text{g L}^{-1}$  of  $\text{Cu}^{2+}$  (five-fold the  $\text{Hg}^{2+}$  concentration) was evaluated. The typical anodic stripping voltammograms revealed that the peak of Hg still overlapped with the Cu peak (Figure 5.7), and so the removal of  $\text{Cu}^{2+}$  is necessary for the determination of  $\text{Hg}^{2+}$  concentrations by this method.

To eliminate  $\text{Cu}^{2+}$ , a conventional off-line SPE cartridge, Analig® TE-3 (GL Sciences, Japan) was used [21, 90]. The voltammograms of the  $20 \mu\text{g L}^{-1} \text{Hg}^{2+}$  solution in the presence of  $\text{Cu}^{2+}$  with and without the SPE pretreatment are shown in Figure 5.7. The voltammogram of standard solution in the presence of  $\text{Cu}^{2+}$  after passage through the SPE cartridge was similar to the voltammogram of the  $20 \mu\text{g L}^{-1} \text{Hg}^{2+}$  solution without  $\text{Cu}^{2+}$ , with a 94-99% ( $n=3$ )  $\text{Hg}^{2+}$  recovery. Therefore, the TE-3 SPE cartridge based pretreatment was effective at removing  $\text{Cu}^{2+}$  from the solution without any significant effect on the determination of the  $\text{Hg}^{2+}$  concentration. In addition, the TE-3 particles (binding capacity = 0.1-0.3 mmol/g) can be reused and the cartridge can be regenerated by eluting  $\text{Cu}^{2+}$  with three bed volumes of 8 M acid solution or 2 M of  $\text{NH}_3$  pH 9.5-10.0 buffer solution.





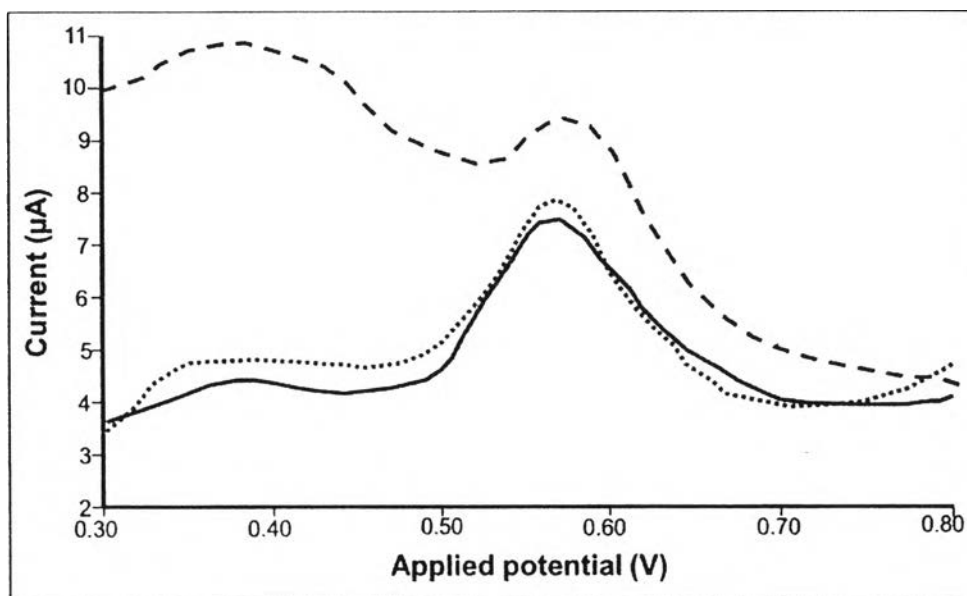


Figure 5.7 Typical square wave anodic stripping voltammograms on the *in-situ* Au-SPCE of  $20 \mu\text{g L}^{-1} \text{Hg}^{2+}$  alone (solid line), or supplemented with  $100 \mu\text{g L}^{-1} \text{Cu}^{2+}$  without (dashed line), or with after pretreatment using a TE-3 SPE cartridge (dotted line).

### 5.3.7 Determination of $\text{Hg}^{2+}$ in Real Samples

Three typical real samples of bottled drinking water, sea water (from South-Pattaya Beach, Thailand) and a  $200 \text{ g L}^{-1}$  table salt solution (>97% by weight sodium chloride), each in 1 M  $\text{HNO}_3$ , were analyzed by the proposed method. The drinking water and the sea water were acidified to 1 M  $\text{HNO}_3$  by dilution with 4 M  $\text{HNO}_3$  (resulting in a final sample dilution factor of 1.33). For the saline solution, 2.000 g of anhydrous table salt was dissolved in 10.00 mL of 1 M  $\text{HNO}_3$  (giving an  $\sim 200 \text{ g L}^{-1} \text{NaCl}$  solution) and then filtered through a piece of filter paper (Whatman No.1). All samples were pretreated using the TE-3 SPE cartridge to eliminate  $\text{Cu}^{2+}$  and then analyzed by SI/SWASV with standard calibration method. The results are summarized in Table 5.3. Although the SWASV peak of  $\text{Hg}^{2+}$  was not found in the unspiked samples, the determination of  $\text{Hg}^{2+}$  in the spiked samples by the proposed method showed very good accuracy with a  $\text{Hg}^{2+}$  recovery in a range of 96.0-101%.

Table 5.3 Determination of Hg(II) concentration in real samples by SI/SWASV using *in-situ* Au film SPCE.

Samples	Spiked Hg(II) concentration ( $\mu\text{g L}^{-1}$ )	Found Hg(II) concentration ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Drinking water	-	Not detected	-
	7.00	$7.04 \pm 0.06$	101
	12.0	$11.5 \pm 0.1$	96.0
Sea water	-	Not detected	-
	7.00	$7.02 \pm 0.07$	100
	12.0	$11.9 \pm 0.3$	98.8
Table salt	-	Not detected	-
	10.0	$9.61 \pm 0.28$	96.1

#### 5.4 Conclusions

An automated flow-based device based on a SI system and coupled with SWASV using an *in-situ* Au-SPCE was developed for the determination of  $\text{Hg}^{2+}$  concentrations. Several parameters in the preparation of the *in-situ* Au film on the SPCE and the subsequent electrochemical detection of  $\text{Hg}^{2+}$ , including the two-step deposition potentials and the square wave-wave form, were optimized. On-line medium exchange before the stripping step was appended as a very small step in the sample injection to remove  $\text{Cl}^-$  ions. The flow pattern of the sequentially injected solutions, evaluated in terms of the two-step deposition potentials, did not have a significant effect on the mixing zone of the two solutions and so the ability to segregate the different deposition potentials. This proposed method provides a cost-efficient, simple, convenient, and highly sensitive device for the quantification of  $\text{Hg}^{2+}$  concentrations. The proposed method with a two-step deposition potential and on-



line medium exchange including a SPE cartridge was successfully applied to determine the  $\text{Hg}^{2+}$  concentration in a drinking water sample and in the chloride-rich samples of 75% (v/v) sea water ( $\sim 46 \text{ g L}^{-1}$  salinity) and  $200 \text{ g L}^{-1}$  table salt with good accuracy.

### Acknowledgements

The authors are grateful for the financial support from Thailand Research Fund under the Royal Golden Jubilee Ph.D. Program (PHD/0320/2551) to Eakkasit Punrat and Orawon Chailapakul; the 90<sup>th</sup> Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund); and the Thai Government Stimulus Package 2 (TKK2555) under the Project for Establishment of Comprehensive Center for Innovative Food, Health Products and Agriculture (PERFECTA). Orawon Chailapakul would like to greatly thank to Thailand Research Fund. We greatly appreciate Dr. Robert Butcher for his help in editing the manuscript under the service of the Publication Counseling Unit of the Faculty of Science, Chulalongkorn University.

