Determination of Arsenic (III) by Sequential Injection/Anodic Stripping Voltammetry (SI/ASV) Using *In-situ* Thin Film-Modified Screen-Printed Carbon Electrode (SPCE)

Eakkasit Punrat[1, 2], Suchada Chuanuwatanakul[2], Orawon Chailapakul[2],
Toshio Takayanagi[1], Takashi Kaneta[1], Shoji Motomizu[3]

[1] Graduate School of Natural Science and Technology, Okayama University 3-1-1, Tsushimanaka, Kitaku Okayama 700-8530, Japan
[2] Electrochemistry and Optical Spectroscopy Research Unit,
Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand
[3] Okayama University Incubator 109, Tsushimanaka, Kitaku, Okayama 700-8530, Japan

Abstract

Sequential injection system (SI system) was used for the pretreatment of a carbon electrode in an anodic stripping voltammetry (ASV) for the determination of arsenic (III). In this research, a screen-printed carbon electrode (SPCE) was used; SPCE was prepared in our laboratory by us. In ASV, SPCE was chosen as a working electrode because SPCE is less expensive, easy to use for a flow cell and suitable for thin-film modification method. ASV parameters were optimized with a handy-type potentiostat. The proposed method is one of alternatives for the determination of arsenic (III), which is fast, accurate and precise method with less expensive automated system.

Keywords Sequential injection (SI), Anodic stripping voltammetry (ASV), Arsenic (III), Screen-printed carbon electrode (SPCE), Thin-film modification

1. Introduction

Arsenic is a semi-metal element and is widely distributed in the earth's crust. The contamination of arsenic may be found in surface and ground water which have flowed through arsenic-rich rocks [1]. Arsenic, therefore, is found in ground water more than in surface water [2]. There are several reports about the contamination of arsenic in drinking water in many places of the world, such as in California, Oregon, Massachusetts, Maine, and New Hampshire of U.S., and Great Britain, Thailand, India and especially in Bangladesh [1-3]. Drinking water contaminated with arsenic is, over a long time, unsafe and can cause various human diseases such as dermal damages, respiratory, cardiovascular, gastrointestinal, bladder, genotoxic, mutagenic and carcinogenic effects [3-5]. The guideline concentration of arsenic in drinking water allowed by U.S. Environmental Protection Agency and World Health Organization is limited to be 10 μg L^{-1} [1, 2].

Recently, several techniques for the determination of arsenic have been developed and used: they are atomic absorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), X-ray fluorescence (XRF), capillary electrophoresis (CE), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), and high-performance liquid chromatography coupled with ICP-MS (HPLC-ICP-MS) [6]. Although such techniques, especially ICP-MS, present good sensitivity with a low detection limit, the disadvantages of them are very large, laboratory-based and time-intensive, to require technicians for operation, and the instruments are sophisticated, very expensive for purchase and management.

Anodic stripping voltammetry (ASV) is one of powerful electrochemical techniques because it can provide high selectivity and sensitivity by a deposition step in which the metal ions are reduced to solid state and preconcentrated on the surface of a working electrode before the stripping measurement of accumulated metals [7]. In addition, ASV requires low electric power, is portable and also suitable for automatic operation [8,9].

To improve sensitivity in ASV determination, in most cases, the electrode surfaces and materials are modified by using metals or carbon in nano-size, such as Au-nano-particle-modified glassy carbon electrode [10], Au-modified boron doped diamond electrode [11], Pt nanoparticle modified electrodes [12,13], alloy of Pt-Fe(III) nanoparticle-modified carbon nanotube on glassy carbon electrode [5], and so on.

In this work, the screen-printed carbon electrodes (SPCEs), which are well known as low-cost electrodes, were prepared in our laboratory by hands with template-blocks [14], and compared with the other ones which were made by automatic syringe-printer. An automated pretreatment system, an SI system, was used together with ASV for the determination of As (III). The SI system used is found to be very suitable for ASV and can advance ASV to be carry out with high precision because the flow manifold can be designed well with superior reproducibility of time, sample volume, mixing condition [7, 15, 16], and therefore those parameters lead to reproducible mass transport on electrode surface [17].

The present work is focused on the determination of As (III) and developing its detection technique to determine fast, accurately and precisely with less expensive maintenance, by SI/ASV using *in-situ* modified SPCEs.

2. Experimental

2.1. Reagents

All of solutions and reagents were prepared and diluted with ultrapure water prepared by a Mill-Q Ultrapure Water Purification System (MilliPore, Japan). The metal solutions, such as Pb (II), Cd (II), As (III), Bi (III) and Au (III) solution, were prepared by accurate dilution from each standard stock solution (1000 mg L^{-1} for atomic absorption standard solution, Wako Pure Chemical Industries, Japan).

2.2. Instruments

The SI system used in this work is a model of MGC Auto-Pret MP-014S (MGC Japan), which is controlled with a program of MGC LMPro ver. 2.5. The Auto-Pret system consists of a 2.5 mL syringe pump, an 8-port selection valve (SLV), a 6-port switching valve (SWV) (this is not shown in Fig. 1) and PTFE tubing-holding coil.

The ASV measurement was controlled and carried out using a potentiostat (a PalmSens: Palm instruments), and in ASV measurement with a thin-layer flow cell, an SPCE was used as a working electrode, an Ag/AgCl as a reference electrode and a stainless steel outlet tube as a counter electrode. All experiments were performed at room temperature.

By using the Auto-Pret/ASV system, the sequence steps of procedures for ASV measurement were optimized for each parameter of the deposition and stripping processes. *In-situ* modifying was done on the deposition stage.

2.3. Step sequence

Sequence steps were designed for each stage containing various parameters. Basically, there are two stages for analysis procedure: (1) an *in-situ* modification with deposition stage and (2) stripping/detection stage. The typical example of a step sequence is shown in Table 1. First, two hundred milliliters of 1 M HCl was aspirated through the selection valve into the holding coil, and then the sample solution and 5 mg L^{-1} gold plating solution were aspirated, respectively. After the aspiration step, the selection valve was moved to the port number 1. While syringe pump was dispensing and the
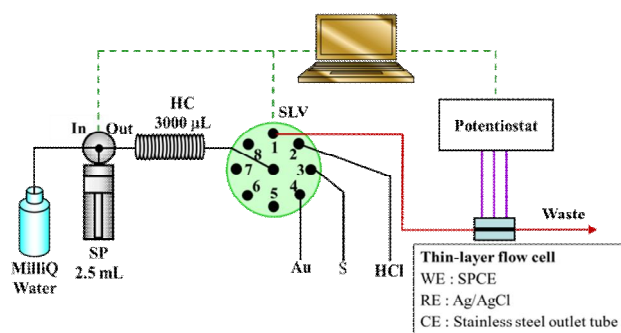

Fig. 1 Schematic diagram of sequential injection (SI) system with anodic stripping voltammetry for *in-situ* gold-film preparation and determination of As (III). SP: syringe pump; HC: holding coil; SLV: 8 port-selection valve; Au: Au (III) plating solution; S: standard/sample solution; HCl: 1 M HCl for flooding of death volume and electrode cleaning solution; WE: working electrode; RE: reference electrode; CE: counter electrode.

deposition potential was applied at -0.5 V *vs.* Ag/AgCl, the lastly aspirated solution which aspirated into the holding coil, the gold plating solution, was forced to flow out from the holding coil into the flow cell at the first stage of the dispense. The dispensing of the solution was continued for 80 s, which were correspond to 800 μL of total aspirated volume, and the dispense solution flowed through the flow cell with a flow rate of 10 μL s^{-1}. The standard solution and 1 M HCl in the holding coil were sequentially dispensed after the gold plating solution. The hydrochloric acid solution in this step was used to flow all of the sample solution that may remain in the tubing connecting between the selection valve and the flow cell. After that, while the pump is stopped, an anodic stripping voltammogram was recorded by linear-sweep voltammetry with the scan rate of 0.3 V s^{-1}. The oxidation reaction occurred in the fresh electrolyte, 1 M HCl flooding solution, whereas the sample matrix, which may interfere with the measurement at the stripping step, was eliminated by this operation. Finally, the electrode cleaning was done with 2.5 mL of 1 M HCl. The cleaning potential was applied at +1 V *vs.* Ag/AgCl. After the cleaning step, next analysis can start automatically.

3. Results and discussion

3.1. Bi(III)- and Au(III)-modified SPCEs for the determination of Cd (II), Pb (II) and As (III)

According to literatures, a square wave (SW) technique for ASV was chosen for the determination of Cd (II), Pb (II) and As (III) representing as heavy metals. Bare SPCEs were chosen as a working electrode at the beginning of the research. The optimum deposition potential for all three analytes is -1.5 V *vs.* Ag/AgCl. Two acidic solutions, HCl and HNO$_3$, at various concentrations were compared each other as a supporting electrolyte. It was found that both acidic solutions can be used favorably. However, by using 1 M HCl as the supporting electrolyte the result showed a lower background and wider potential window at negative voltage.

Bismuth (III) in 1 M HCl solution and Au (III) in 1 M HNO$_3$ were used for modifying SPCEs to simultaneous determination of Cd (II), Pb (II) and As (III). Bismuth (III) and Au (III) were reduced and deposited as a thin film on the surface of SPCEs by applying potential.

It was found that Bi-film SPCE was very useful for the determination of Cd (II) and Pb (II), which show oxidation potentials more negative than that of bismuth. However, Bi-film cannot enhance the signal of arsenic, which shows more positive oxidation potential at which Bi-film was demolished by oxidizing to Bi (III).

Using Au (III) in 1 M HNO$_3$, the blank signal of Au-film

Table 1   Step sequence for the determination of As (III) using *in-situ* gold-plating SPCE

Step	Syringe valve position	SLV position; [Port no.] Description	*Syringe pump Status	Flow rate (μL s^{-1})	**Potentiostat Status
1		[2] 1 M HCl	Asp 200 μL	100	
2		[3] Standard As(III)	Asp 300 μL	100	Standby
3		[4] Au(III) 5 mg L^{-1}	Asp 300 μL	100	
4	OUT	[1] Flow cell	Dis 800 μL	10	E_{dep} = -0.5 V
5		-	Delay 30 s	-	LSASV (scan rate = 0.3 V s^{-1})
6		[2] 1 M HCl	Asp 2500 μL	100	E_{clean} = +1 V
7		[1] Flow cell	Dis 2500 μL	50	

*Asp: aspirate; Dis: dispense;

**LSASV: linear-sweep anodic stripping voltammetry; E_{dep}: deposition potential; E_{clean}: cleaning potential;

SPCEs have a broaden peak overlapping with an oxidation peak of As (III). This overlapping peak was not appeared when the linear sweep voltammetry was used (see in 3.5). As a result, the Au-film SPCE was chosen for arsenic measurement as a working electrode in the further experiment.

3.2. Cleaning condition for completely removing of remaining active species

After the measurement, the surface of working electrode should be cleaned by removing of remaining species, such as metal-analytes and modified metal. One molar concentration of HCl and HNO_3 solution was tested as a cleaning solution, which was used in the step 6 and 7 of Table 1. The voltammetric scanning potential was done after the cleaning step in pure electrolyte solution for checking blank signal. If the cleaning was well done, there should be no peak of any metal in the blank signal.

It was found from the experiment that an HCl solution was more suitable than that of HNO_3. It was demonstrated that since chloride ion could induce the formation of metal-chloride complexes/compounds, the accumulated metals were easily oxidized. In addition, the broaden peak, which was similarly found in voltammogram of Au (III) in 1 M HNO_3, and was mentioned in 3.1, was observed to be grow, when HNO_3 was used. This means that the use of HNO_3 should be avoided. In this case, it may be supposed that HNO_3 may oxidize some species on the surface of the electrode.

Further, the flow rates of cleaning step were studied by varying the flow rate: 10, 20 and 50 $\mu L\ s^{-1}$. The best flow rate for cleaning is found to be 50 $\mu L\ s^{-1}$.

3.3 Comparison of SPCEs made by different techniques

Silver-electrical contact, which was made by using hand-screen silver ink and gold-electrical contact, which was made by chemical-vapor deposition (CVD), were compared by using SWASV. Both electrodes gave nearly similar sensitivity. However, SPCEs with the silver-electrical contact often showed a little smaller peak at about +0.15 V *vs.* Ag/AgCl that may overlap the oxidation peak of arsenic, and is appeared at about +0.2 V *vs.* Ag/AgCl. Such an unfavorable peak was presumed to be an oxidation peak of silver from the silver-electrical contact screened lower layer of the surface of the carbon electrode. So, the gold-electrical contact was chosen in the following research.

Two techniques for the preparation of the carbon surface also were studied. Of these, one is a hand-screen printing technique with a template-block, and the other is a programmed printing technique with a syringe-printer following this step. First, the carbon ink, which has high viscosity, was diluted with an ink solvent, and then it was filled into a syringe (like an ink injector). The pattern of carbon printing was designed in a rectangular
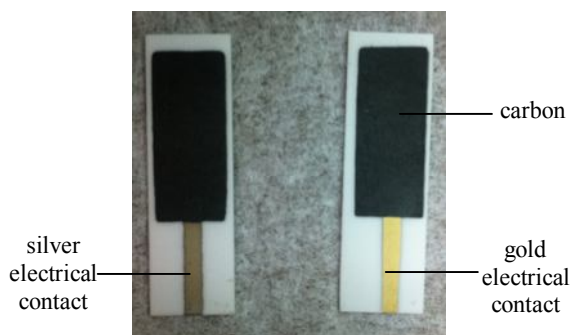
shape with 2.1 cm length and 1 cm width. The length of printing can be controlled via software but the printing width was controlled by the size of syringe needle. The size of needle used in this pattern is 600 μm (equal to 0.6 mm). For one step of printing, the syringe moved in U-shape, which means that the carbon ink was printed in the size of 2.1 cm length x 1.2 mm width (twice of syringe-needle size). The printing has done in 8 steps, so the width is 8 times and equal to 9.6 mm (~1 cm). The electrodes were put on the hot plate at the temperature of 60ºC to dry after each printing. The drying process needed about 45 minutes. When the electrode was dried, the carbon printing was started on the same path. This printing was done 4 times. So, the electrodes have rough surface following the path of printing. Although the SPCE made by the syringe printer gave higher sensitivity, the SPCE made by the hand-screen printing technique gave more repeatability, and could prepare many electrodes at once. Therefore, the hand-screen printing technique was chosen for printing carbon.

3.4 Electrochemical behavior in cyclic voltammetry (CV)

CV study of three different SPCEs, such as a bare SPCE, a Bi-film SPCE and an Au-film SPCE, in a solution containing 10 mg L^{-1} of As (III) was carried out. There was no oxidation peak of arsenic in the voltammograms of the bare SPCE and Bi-film SPCE. The Bi-film SPCE was found to be inadequate and could not be used to enhance the sensitivity of As (III) determination, because bismuth was oxidized at potential of -0.2 V, which is more negative potential than the oxidation potential of arsenic. This showed that Bi-film was destroyed before arsenic will be measured.

Voltammograms in Fig. 3 showed the results of the study of gold-modifying on SPCE. The peak of arsenic appeared at the reduction potential of -0.37 V, which is the oxidation potential of +0.20 V *vs.* Ag/AgCl. These peak potentials agreed with Brusciotti and Duby's research [18]. An oxidation peak, which appeared at about +1.1 V, was proposed by Brusciotti and Duby as an oxidation peak of As (III) to As (V). However, the oxidation peak at potential +1.14 V, as is shown in Fig. 3, occurred in the solution, in which there is no arsenic (dash line), and the height of such peak was nearly equal between two solutions: a solid line (As(III) 10 mg L^{-1} / Au(III) 5 mg L^{-1}) and a dash line (Au(III) 5 mg L^{-1}). As the result from the present experiments, it was concluded that this peak is caused to
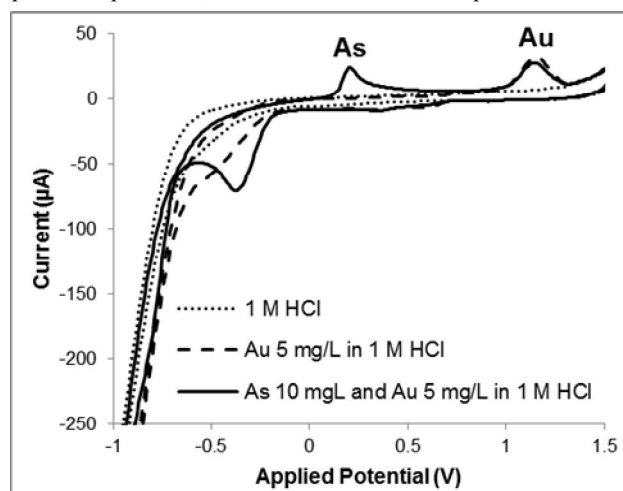
Fig. 3 Cyclic voltammograms on SPCE in different solutions using 1 M HCl as supporting electrolyte. CV's potential range is -1.5 to +1.5 V *vs.* Ag/AgCl, potential step is 10 mV and scan rate is 0.1 V s^{-1}.

Fig. 2 A SPCE with silver electrical contact (left) and a SPCE with gold electrical contact (right) were prepared by ourselves.

an oxidation peak of gold.

3.5 Electrochemical ASV techniques for determination of As (III)

Three techniques of voltammetric scan, such as linear sweep (LS), differential pulse (DP) and square wave (SW), were applied to the determination of As (III) via ASV method.   Only in the voltammograms of LS-ASV, an oxidation peak of As can be observed at potential of +0.24 V   *vs.* Ag/AgCl.

Furthermore, 30 times of the measurement by LS-ASV without cleaning of gold film were done, where gold film was prepared only in the first measurement, and then only standard As(III) solution was injected to the system and measured. It was found that the sensitivity decreased slightly in long term measurement with a relative standard deviation (RSD) of 6.3% and 9.9% in 20 and 30 times of measurement, respectively (see in Fig. 4(a)). To improve the reproducibility, the method with renewing of gold-film SPCE was examined for comparison. Various peak height corresponding to the oxidation of As (III) was observed by using potential scan rate of 0.30 V s^{-1}.   Using As (III) at concentration of 3 mg L^{-1}, the average peak height was 8.33±0.22 µA and RSD is 2.6% (n=17) (see in Fig. 4(b)). From these results, the method with renewing of the gold-film preparation is recommended and very useful for improving reproducibility of the measurement.

3.6 Optimization of parameters for the determination of As (III) using the method with in-situ gold plating SPCE

3.6.1 Potential scan rate

Several potential-scan rates were examined; they were 0.02, 0.03, 0.05, 0.10, 0.30, 0.50 and 1.00 V s^{-1}. Triplicate measurements for each rate were carried out.   Preferably in low potential scan rate, the delay time in the step 5 of the step sequence in Table 1 was changed to 60 s for waiting the completion of the ASV measurement before the cleaning step
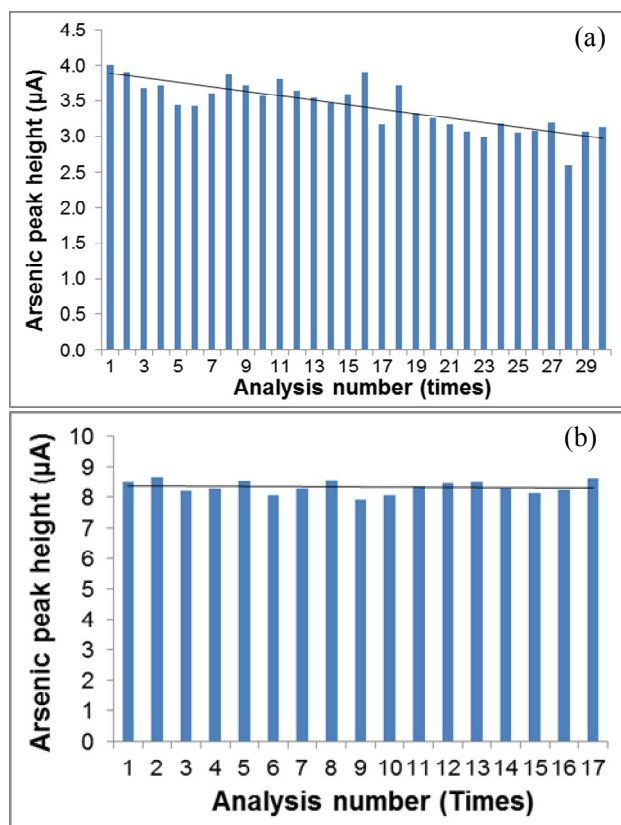

Fig. 4 Bar-graph of the determination of As (III) at the concentration of 3 mg L^{-1} in 1 M HCl by LS-ASV without cleaning and re-preparation of gold-film (a) and using *in-situ* gold-film (b) plotted between number of analysis time and anodic stripping peak height of arsenic.
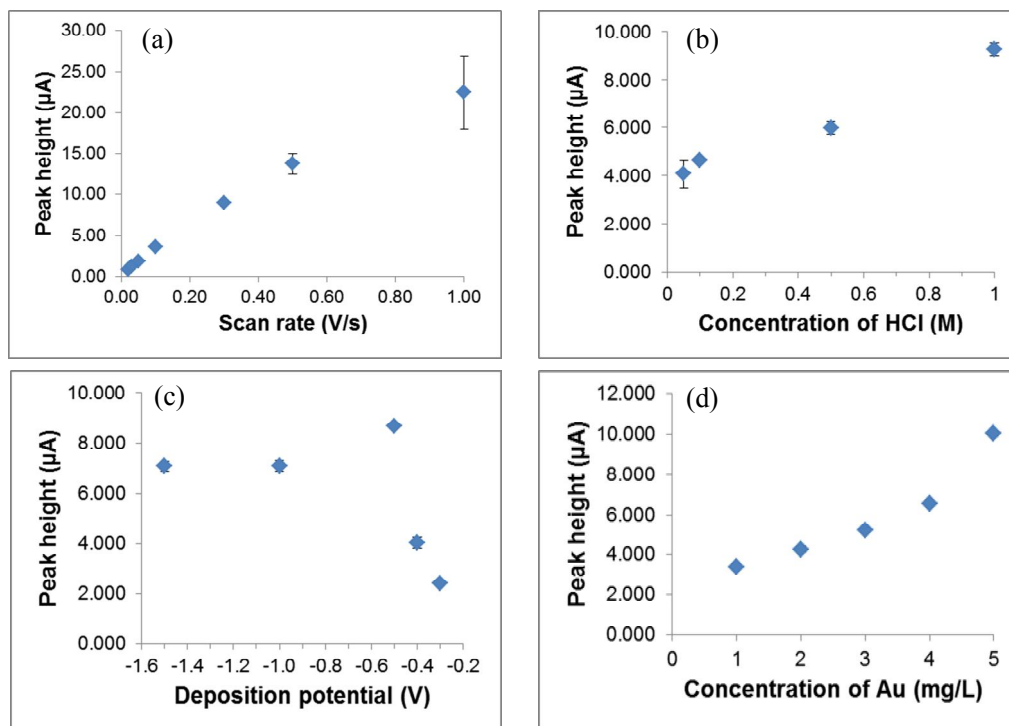

Fig. 5   Effects of potential scan rate (a), supporting electrolyte's concentration (b), deposition potential (c) and concentration of gold plating solution (d) on linear sweep anodic stripping peak current of solution containing 3 mg L^{-1} of As (III) in 1 M HCl (standard deviations were included).

was started.

The effect of the potential scan rate was shown in Fig. 5(a). With an increase in the scan rate, the peak height also increased, and also noise signal increased. Standard deviations were so large at the fast scan rates. As a compromise between sensitivity and noise, the optimal condition was determined to be 0.30 m vs.$^{-1}$.

3.6.2 Concentration of supporting electrolyte

From the section 3.2, HCl was used as the supporting electrolyte. The effect of the concentrations of HCl was examined by varying the concentrations: they were 0.05, 0.1, 0.5 and 1 M. Other solutions, such as standard As (III) solutions and Au (III) plating solution, were prepared by making up the volume with the optimal concentration of HCl. However, the cleaning solution was fixed to 1 M HCl. In addition, the higher concentration than 1 M was not studied because hydrogen gas was generated easily and the electrode surface was corroded in acid. Fig. 5(b) shows that the concentration of 1 M of HCl solution gave the best result.

3.6.3 Deposition potential

Deposition potential is an applied potential for the preparation of the gold-film on SPCE. Gold (III) ion in the solution can be reduced to it solid state on the SPCE. Furthermore, this potential has a very important function as the preconcentration potential of arsenic on the gold film.

The deposition potentials examined in this work were -1.5, -1.0, -0.5, -0.4, -0.3 V *vs.* Ag/AgCl. These values were chosen, and were started at a highly negative potential of -1.5 V, at which most of metal ions, such as Pb (II), Cd (II), Zn (II), Bi (III), As (III) and Au (III), can be reduced and then deposited on SPCE [3,7,14,18]. However, this research is focused on the determination of As (III) by using the gold-film SPCE, and therefore the deposition of other metals, which need high negative potential, can be ignored.

In the case of high negative potential, the hydrogen evolution occurred by the competition with the reduction of metals, and further generated hydrogen gas may block some areas of electrode surface and then an active surface will be abated. On the other hand, in case of low negative potential, the potential was not enough to reduce metal ions. As the optimal deposition potential, -0.5 V *vs.* Ag/AgCl was selected from the result shown in Fig. 5(c).

3.6.4 Effect of concentration of gold plating solution

The concentration of a gold plating solution will guide the area and the thickness of the gold film prepared by electrochemical deposition on SPCE. The concentration of 5 mg L^{-1} of Au (III) was the maximum concentration used for the preparation of the gold film, which could be removed by using 2.5 mL of 1 M HCl with a flow rate of 50 μL s^{-1} and a cleaning potential of +1 V *vs.* Ag/AgCl. This means that if the concentration more than 5 mg

L^{-1} was used, the carry-over effect was observed. Therefore, the concentrations of the gold plating solution were examined by using 5 mg L^{-1} and lower. The concentration of 5 mg L^{-1} was chosen from the results shown in Fig. 5(d).

3.7 Optimal conditions for As (III) measurement using SI/ASV method

Important conditions, not only electrochemical detection parameters, but also kinds of modifying metal and parameters about how to clean electrode surface, were studied. Optimal conditions for the determination of As (III) using SI/ASV method were summarized in Table 2.

3.8 Measurement method for the determination of As (III)

Finally, typical experiments for determination of As (III) were done at several concentrations between 1 and 100 mg L^{-1}. The step sequence was used following Table 1 and other conditions were used following Table 2. The analytical performances of this method were studied.

Limit of detection was calculated from 3 times of standard deviation (3SD) of signal of low concentration as 1 mg L^{-1}. The limit of detection was 0.1 mg L^{-1}. Furthermore, the reproducibility of the propose method was very good as RSD of 2.6% (n=17). The typical voltammograms were shown in Fig. 6.

4. Conclusion

An automated flow-based system, SI system coupled with LS-ASV for the determination of As (III) using *in-situ* gold-film SPCE has been developed. Fundamental study about parameters of gold-film preparation and electrochemical techniques were optimized. The proposed system will become
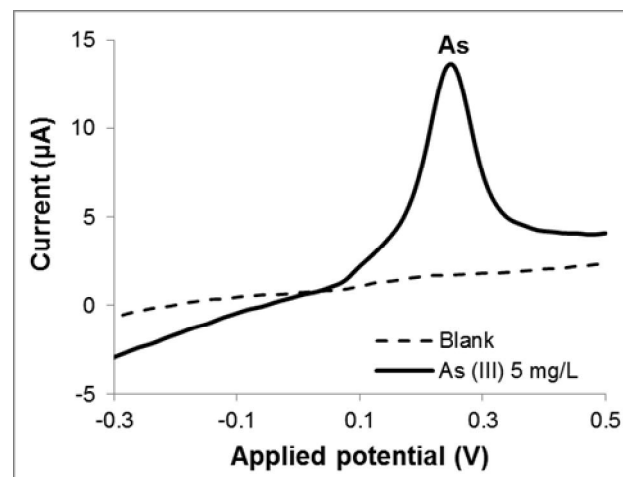

Fig. 6 Typical linear sweep voltammogram of solution containing As (III) 5 mg L^{-1} in 1 M HCl using *in-situ* gold-film SPCE by SI system controlled by following the step sequence in Table 1. Electrochemical parameters and others were used at optimal conditions shown in Table 2.

Table 2 Optimal conditions for As (III) measurement using SI/ASV method

Condition	Examined values	Optimum
Kinds of metal modifying on SPCE	Bi (III) and Au (III)	Au (III)
Cleaning Solution	1 M HCl and 1 M HNO$_3$	1 M HCl
Cleaning flow rate (μL s^{-1})	10, 20, 50	50
Voltammetry techniques	Linear sweep, Differential pulse, Square wave	Linear sweep
Potential scan rate (V s^{-1})	0.02, 0.03, 0.05, 0.10, 0.30, 0.50, 1.00	0.30
Concentration of supporting electrolyte; HCl (M)	0.05, 0.1, 0.5, 1	1
Deposition potential (V)	-1.5, -1.0, -0.5, -0.4, -0.3	-0.5
Concentration of Au(III) (mg L^{-1})	1, 2, 3, 4, 5	5

an alternative method for As (III) determination. The advantages of the proposed SI/ASV method are: (1) sample consumption for the detection of As(III) is very low and as low as 0.3 mL with the detection limit of 0.1 mg L^{-1} of As (III), (2) the tedious pretreatment can be carried out automatically by a computer-controlled automated system, (3) the reproducibility can be improved by the reproducible pretreatment and by using cleaning a gold-film on the SPCE, (4) SPCEs can be prepared by us, and are very stable and reproducible, (5) the cost performance of the electrode, ASV and other systems necessary for the measurement is very good, and (6) the portability is very good, and therefore on-site measurement can be easily carried out.

Though the proposed SI/ASV method has many advantages compared with other methods such as spectroscopic methods, chromatographic methods etc, the sensitivity for As measurement is not enough for WHO guideline. As is well known, however, the sensitivity in ASV technique can be easily improved by increasing sample volumes and enriching the analyte on the surface of SPCE, and also it can be improved by using mini-column enrichment techniques which will be installed in the present SI system, though sample volumes necessary for the determination of arsenic must be increased to several milliliters.

Acknowledgement

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