



Method development for the determination of arsenic by sequential injection/anodic stripping voltammetry using long-lasting gold-modified screen-printed carbon electrode[☆]

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ABSTRACT

An automated method has been developed for determining the concentration of inorganic arsenic. The technique uses sequential injection/anodic stripping voltammetry with a long-lasting gold-modified screen-printed carbon electrode. The long-lasting gold electrode was electrochemically deposited onto a screen-printed carbon electrode at a potential of -0.5 V vs. Ag/AgCl in a supporting electrolyte solution of 1 M hydrochloric acid. Under optimal conditions and the applied potentials, the electrode demonstrated that it can be used for a long time without a renewal process. The linear range for the determination of arsenic(III) was 1 – 100 $\mu\text{g L}^{-1}$, and the limit of detection (LOD) in standard solutions was as low as 0.03 $\mu\text{g L}^{-1}$ for a deposition time of 120 s and sample volume of 1 mL. This method was used to determine the concentration of arsenic(III) in water samples with satisfactory results. The LOD in real samples was found to be 0.5 $\mu\text{g L}^{-1}$. In addition, speciation between arsenic(III) and arsenic(V) has been achieved with the proposed method using deposition potentials of -0.5 V and -1.5 V for the determination of the arsenic(III) concentration and the total arsenic concentration, respectively; the results were acceptable. The proposed method is an automated system that offers a less expensive alternative for determining trace amounts of inorganic arsenic.

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1. Introduction

Arsenic (As) is a semi-metal element with a name that originated from the Greek word *arsenikon*, which means mighty. It is a natural element found in the Earth's crust. The contamination of ground and surface water with As commonly occurs when water flows through As-rich rock. The contamination of ground water used for drinking with As is a serious global concern. Several locations on Earth, such as Bangladesh, India, Taiwan, Great Britain, Thailand, and within the US (including Hawaii, California, and New Hampshire), have reported environmental water contamination with As [1–5].

[☆]This article is dedicated to Professor Dr. Kate Grudpan (Chiang Mai University, Thailand) in celebration of his 60th birthday.

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The majority of As species found in the environment are in inorganic forms, such as As(V), As(III), As(0) and As(-III). Importantly, the different forms of As show various hazard levels. The inorganic As species can be more toxic than the organic As species [6]. Furthermore, As(III) is reported to be found more than As(V), and As(III) is significantly more toxic and soluble than As(V) [7]. Chronic exposure to arsenic is known to cause a variety of adverse health effects in humans including dermal changes and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic, and carcinogenic effects [8,9]. The maximum arsenic concentration allowed in drinking water by the US Environmental Protection Agency and the World Health Organization is 10 $\mu\text{g L}^{-1}$ [10,11]. Therefore, As monitoring the environmental analysis is extremely important.

To evaluate the As level in drinking water, several methods have been developed, as summarized in reviews [12–15]. These methods include inductively coupled plasma-mass spectrometry (ICP-MS), high performance liquid chromatography with ICP-MS, graphite furnace atomic absorption spectrometry and atomic

fluorescence spectrometry. However, these methods use large instruments and are only suitable for laboratory use. Furthermore, the most reliable methods are time-consuming. Because of these factors, these methods are not useful for the large number of samples present in fieldwork. Thus, a rapid and portable detection method needs to be developed. Electrochemistry provides several attractive and low cost techniques as possible ways to solve these problems [16,17].

Anodic stripping voltammetry (ASV), which has been known to chemists for more than 50 years, is one of these powerful techniques for metal analysis. It provides extremely high sensitivity and a very low detection limit with short analysis times [18]. The basic process of ASV for the determination of trace metals involves the electrochemical deposition of metals onto a suitable electrode at a more negative potential than the standard potential of the metal of interest for a few minutes. After this deposition, the accumulated metals on the electrode surface are oxidized into solution using a reverse potential scan.

Using differential pulse ASV for the determination of arsenic, Forsberg and collaborators investigated various working electrode materials including mercury (Hg), platinum (Pt), gold (Au) and silver (Ag) [19]. Their results found that Au has a larger hydrogen overvoltage than Pt. The oxidation peak of Au further is at high positive potential of about +0.9 V vs. Ag/AgCl, while the oxidation peak potentials of Ag and Hg are close to the oxidation peak potential of As. Therefore, Au is a suitable material for arsenic determination using ASV. Moreover, there have been several reports on Au electrodes or Au-modified electrodes for As determination [19–21]. Some apparent problems of ASV with Au solid electrode are an unexpected stripping signal and a decrease in sensitivity. These are mainly solved by polishing and washing the electrode in batch experiments. As a result, this extra processing is an impediment to high-throughput analysis. However, many researchers have focused on the modification of electrodes using renewable gold films [22,23]. The renewal of a gold film before each measurement was found to be a way to improve reproducibility. Thus, in the current work, we successfully used gold modified by electrochemical deposition on a screen-printed carbon electrode (SPCE) for As determination.

To promote the automation of As detection, this work has used ASV coupled with a sequential injection (SI) system. An SI system is a very versatile, automated flow-based system and has been found to be compatible with a large number of detection devices. An SI system gives very good precision and reproducibility and presents the possibility for the automation of the tedious procedures needed in routine analysis [24,25]. The SI system can be successfully coupled to ASV. The flow stream present in the deposition step of ASV leads to high and reproducible mass transport of metal ions onto electrode surface [26]. Numerous research papers about metal determination using ASV coupled to SI systems have been published. An SI system has also been used for the *in-situ* preparation of bismuth film [18,27] and antimony film [28].

Our previous work determined the As(III) concentration using coupled SI/ASV and *in-situ* Au film modified on SPCE [29]. However, the limit of detection was insufficient for quantitative As detection in environmental analysis. On the one hand, renewal of the Au-film was limited by the amount of Au on the electrode surface; a large amount of Au resulted in incomplete cleaning. The previous work showed that it was possible to renew the Au-film SPCE *in situ*. On the other hand, a large amount of Au on the SPCE led to an increase in roughness and surface area, which allows for a lower As detection limit. The current study, therefore, presents a different solution for the determination of the inorganic As concentration using SI/ASV with an Au-modified SPCE. The experiments were performed under simple test conditions to maintain the lifetime of the modified Au on the SPCE without the need for the renewal process. A large linear range between 1 and

100 $\mu\text{g L}^{-1}$ was achieved and the lowest value of the detection limit (3S/N) obtained was 0.03 $\mu\text{g L}^{-1}$. The proposed method was successful in assessing the As concentration in the real water samples.

2. Experimental

2.1. Reagents

The As(III) and Au(III) standard solutions were prepared using accurate dilution from each standard stock solution (1000 mg L^{-1} for the atomic absorption standard solution, Wako Pure Chemical Industries, Japan) with 1 M HCl. The electrolyte solution, 1 M HCl, was prepared by the appropriate dilution of a 35.0–37.0% hydrochloric acid solution (Kanto Chemical, Japan). Ultrapure water was prepared by a Milli-Q Ultrapure Water Purification System (MilliPore, Japan) and used for the preparation of all of the reagent and standard solutions.

In the interference study section, nine cation solutions were prepared by dilution from each standard stock solutions (1000 mg L^{-1} for the atomic absorption standard solution, Wako Pure Chemical Industries, Japan): NaCl, CaCO_3 , MgCl_2 , CdCl_2 , Pb (NO_3)₂, NiCl_2 , $\text{Cu}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and $\text{Fe}(\text{NO}_3)_3$. And seven stock solutions of each anion were prepared by dissolving the following sodium and potassium salts (analytical grade, Wako Pure Chemical Industries, Japan): NaCl, NaBr, Na_2SO_4 , NaH_2PO_4 , $\text{NaOAc} \cdot 3\text{H}_2\text{O}$, Na_2CO_3 , and NaNO_3 .

2.2. Screen-printed carbon electrode (SPCE)

The SPCEs were prepared in two steps. First, gold conductive pads were deposited on ceramic substrates using chemical vapor deposition (CVD). Five nanometers of chromium were used as an adhesive layer between the substrate and the gold pad. The thickness of the gold conductive pad was 50 nm. After the deposition, carbon ink (Electrodag PF-407C, Acheson, USA) was screen-printed onto the gold conductive pads and dried in an oven at 80 °C for 2 h.

2.3. Apparatus

The SI system used in this research was an Auto-Pret system (MGC Auto-Pret MP-014S, MGC Japan), which was consisted of a syringe pump, an 8-port selection valve, a switching valve (not used in this research), a PTFE holding coil and other connectors and tubing. This system can be computer-controlled via the MGC LMPro ver. 2.5 software.

The electrode modifications and electrochemical measurements were carried out in a radial flow cell (MF-1901, Bioanalytical Systems, USA) using a portable potentiostat, PalmSens (PalmSens BV, The Netherlands). The flow cell consisted of a silicon gasket with a thickness of 0.5 mm as a spacer and a three electrode systems with an Au-modified SPCE as the working electrode, a Ag/AgCl electrode (3 M KCl) as the reference electrode, and a stainless steel outlet tube as the counter electrode.

2.4. Procedure

A schematic diagram of the SI/ASV system with the gold-modified electrode used for the determination of arsenic is shown in Fig. 1. A step sequence for the Au modification on the electrode and a sequence for the determination of the arsenic concentration are shown in Tables 1 and 2, respectively.

The electrolyte solution and the Au(III) solution were sequentially aspirated into the holding coil and then dispensed into the flow cell in which the Au(III) was reduced and deposited onto the SPCE at -0.5 V vs. Ag/AgCl. The electrolyte solution, 1 M HCl, was

used for the displacement of dead volume in the tubing between the SI system and the flow cell. The volume of the syringe is 2.5 mL. The minimum volume of the Au(III) solution required for the gold modification, however, was more than 2.5 mL (see Section 3.1). Therefore, the injection of the Au(III) solution was repeated using step 3–4 in Table 1. The total time for modification of Au, including delay-time from valve position changing, is about 20 min. The gold-modified SPCE was used and kept in a solution containing 1 M HCl during the entire experiment.

To determine arsenic concentration, the sample solution and the displacement solution were sequentially injected into the flow cell. As (III) was deposited onto the Au-modified SPCE at -0.5 V vs. Ag/AgCl. After the SI system was stopped for a 5-s equilibration time, the linear

sweep voltammogram was recorded from -0.5 to $+0.4$ V vs. Ag/AgCl. The other parameters shown in Table 3 have been reported elsewhere [29]. Finally, the Au-modified SPCE was cleaned to remove any remaining analyte at a potential of $+0.4$ V vs. Ag/AgCl under a stream of 1 M HCl for 120 s (step 5 in Table 2). The standby potential was set to $+0.4$ V vs. Ag/AgCl; at this potential, the gold on the SPCE remained on the SPCE. The total analysis time for the determination of As, including the cleaning step and delay-time from valve position changing, is only 6 min for each measurement. All experiments were performed at room temperature (23 – 28 °C).

3. Results and discussion

3.1. The effect of the amount of Au on the modified SPCE

In this work, a SPCE was modified with gold by electrolysis. The Au(III) solution was injected into the flow cell and an optimal deposition potential of -0.5 V vs. Ag/AgCl was applied to the SPCE to deposit the gold. The Au-modified SPCE was used for the determination of As(III) by SI/ASV. After the voltammogram was

Table 3

Optimized experimental conditions for determination of As(III) using SI/ASV [29].

Parameter	Optimized value
Cleaning solution	1 M HCl
Cleaning flow rate	$50 \mu\text{L s}^{-1}$
Potential scan rate of linear sweep voltammetry	0.30 V s^{-1}
Supporting electrolyte	1 M HCl
Deposition potential	-0.5 V
Concentration of the Au(III) modifying solution	5 mg L^{-1}

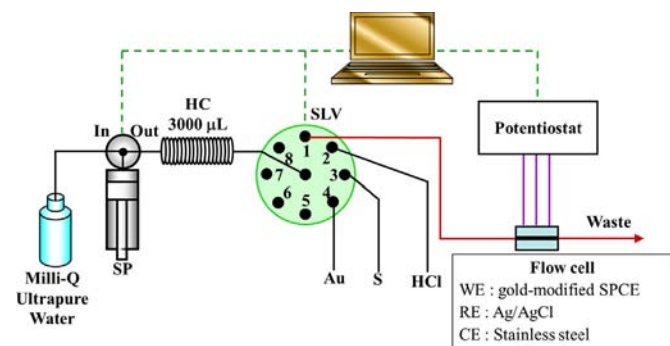


Fig. 1. Schematic diagram of the SI/ASV used for the electrode modification and the determination of the arsenic concentration (SP, syringe pump; HC, holding coil; SLV, 8-port selection valve; Au, Au(III) modifying solution; S, standard/sample solution; HCl, 1 M HCl for displacement of the dead volume and the electrode cleaning solution; WE, working electrode; RE, reference electrode; and CE, counter electrode).

Table 1

Step sequence for Au modification of the SPCE by electrolysis using SI system.

Step	Operating description	Selection valve position [port number]	Syringe pump status	Volume (μL)	Flow rate ($\mu\text{L s}^{-1}$)	Electrode potential (V)
1	Aspirate Au(III) solution into the holding coil	[2] 1 M HCl [4] Au(III)	Aspirate	200	100	$+0.4^a$
2	Dispense the Au(III) solution into the flow cell for the modification of Au on SPCE	[1] Flow cell	Aspirate Dispense	2300 2500	100 10	$+0.4^a$ -0.5
3	2nd aspiration of the Au(III) solution into holding coil	[2] 1 M HCl [4] Au(III)	Aspirate	200	100	-0.5
4	2nd dispensing of the Au(III) solution into the flow cell for the modification of Au on SPCE	[1] Flow cell	Aspirate Dispense	2300 2500	100 10	-0.5 -0.5

^a Standby potential.

Table 2

Step sequence for determination of As(III) using SI/ASV.

Step	Description	Selection valve position [port number]	Syringe pump status	Volume (μL)	Flow rate ($\mu\text{L s}^{-1}$)	Electrode potential (V)
1	Aspirate the sample solution into the holding coil	[2] 1 M HCl [3] Sample	Aspirate	200	100	$+0.4^a$
2	Dispense the sample solution into the flow cell for the deposition of As	[1] Flow cell	Aspirate Dispense	1000 1200	100 10	$+0.4^a$ -0.5
3	Equilibration	–	Delay ^b	–	–	-0.5
4	Stripping and recording the voltammogram	–	Delay ^b	–	–	Scan (-0.5 to $+0.4$)
5	Cleaning the electrode	[2] 1 M HCl [1] Flow cell [2] 1 M HCl [1] Flow cell	Aspirate Dispense Aspirate Dispense	2500 2500 2500 2500	100 50 100 50	$+0.4^c$ $+0.4^c$ $+0.4^c$ $+0.4^c$

^a Standby potential.

^b Total delay time 30 s.

^c Cleaning potential.

recorded, the SPCE was cleaned at potential of +0.4 V vs. Ag/AgCl to remove any remaining arsenic. At the cleaning potential, the Au remained on the SPCE. The electrode was used as the working electrode several times (for more detail, see Section 3.2).

The amount of Au on the modified SPCE affected the anodic stripping peak current of As. The amount of Au on the SPCE could be controlled by altering the concentration of the Au(III) solution and the deposition time. The effect of the amount of Au on the modified SPCE has been investigated for the various deposition times by changing the volume of the Au(III) solution and using the same flow rate and the same concentration of the Au(III) solution (5 mg L^{-1}). The voltammograms of a solution containing 3 mg L^{-1} of As(III) in 1 M HCl were recorded. The peak potential of the linear sweep anodic stripping of As is +0.2 V vs. Ag/AgCl. The results are shown in Fig. 2. The stripping peak current of As dramatically increased at small volumes of the Au(III) solution and slightly increased at large volume of the Au(III) solution. The minimum recommended volume of the Au(III) solution for electrode modification was 3.3 mL. The syringe pump used in this work, however, has a volume limit of 2.5 mL, so the Au(III) solution was injected into the flow cell twice as shown in Table 1. Therefore, 4.6 mL of the Au(III) solution was chosen for the determination of As(III) in this work.

3.2. Stability of the Au-modified SPCE

In the previous work [29], the cleaning potential was set to +1.0 V vs. Ag/AgCl; at this potential, both the remaining As and the deposited Au were oxidized and stripped from the electrode surface. The sensitivity of the Au-modified SPCE without renewal of the Au layer decreased slightly over the course of the experiment and had a relative standard deviation (RSD) of 9.9%. However, renewal of the Au layer on the SPCE has been achieved and the determination of the As(III) concentration had a detection limit of 0.1 mg L^{-1} and RSD of 2.6% ($n=17$). This work tried to improve the sensitivity of the As(III) detection and to develop the long-lasting property of Au-modified SPCE. The cleaning potential and the standby potential were changed to +0.4 V vs. Ag/AgCl. At this potential, only the As was oxidized and stripped from the electrode surface, while the Au remained and was long lasting.

To confirm that the Au-modified SPCE in this work was long-lasting, the voltammograms of a solution containing 3 mg L^{-1} As (III) in 1 M HCl were recorded several times without renewal of the Au layer. The electrode was modified using 0.3 mL of the Au (III) solution because the electrode fouling can be easily followed up by the small volume. Typical voltammograms of As are shown in Fig. 3. The stripping peak current of As in the voltammograms was the same even after the Au-modified SPCE was used several

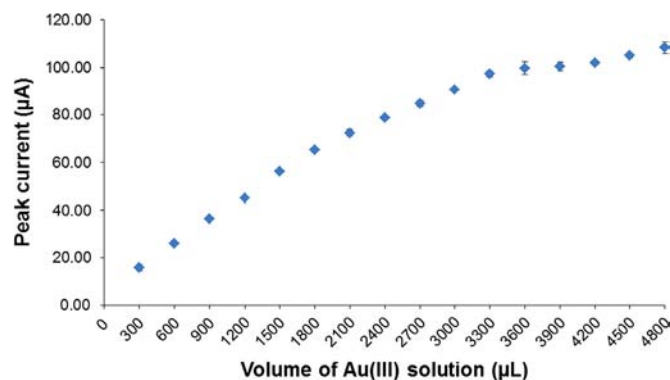


Fig. 2. The effect of the amount of Au on the modified SPCE demonstrated through the effect of the volume of the Au(III) solution on the As stripping peak current of a solution containing 3 mg L^{-1} As(III) in 1 M HCl.

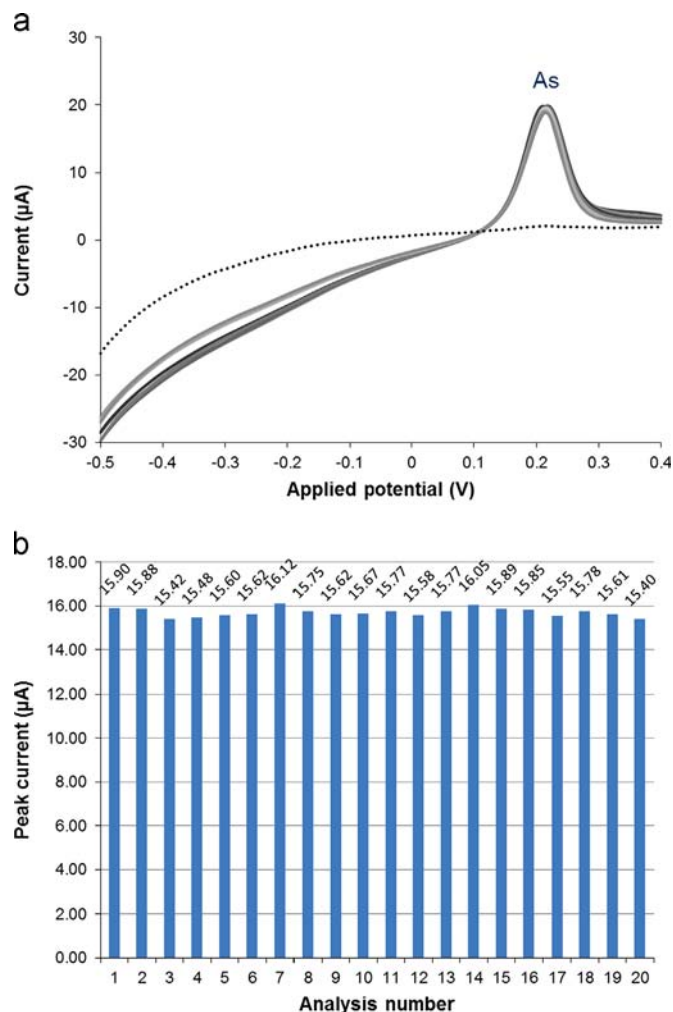


Fig. 3. (a) Typical linear sweep anodic stripping voltammograms (the dotted line is a voltammogram of the blank solution) and (b) the anodic stripping peak currents of the 20 analysis times on the Au-modified SPCE of a solution containing 3 mg L^{-1} in 1 M HCl using an Au(III) solution volume of 0.3 mL for the modification of SPCE without renewal of the Au layer.

times. The RSD was found to be 1.2% ($n=20$). Furthermore, the Au-modified SPCE can be kept in a 0.1 M HCl solution when it is not in use. The Au-modified SPCE was used to record voltammograms of a solution containing 3 mg L^{-1} As(III) for more than 300 measurements, which were carried out for 3 days, with the similar stripping peak current of As (RSD=2.7%). While the experiments were performed at room temperature which typical varied from 23°C to 28°C from morning to evening, the stripping current was not significantly affected by these temperature variations. The Au-modified SPCE has been shown to be long-lasting.

3.3. Microscopic images

Microscopic images of the electrode surface were taken using a digital optical microscope (digital microscope VHX 1000, Keyence Corporation, Japan). First, images of the bare SPCE were taken. A typical image is shown in Fig. 4(a). Then, the electrodes were modified with Au by electrochemical deposition using the sequence in Table 1. Images of the Au-modified SPCEs were taken (Fig. 4(b)). The yellow color in the figure is Au deposited on the electrode surface, while the black zones are a part of the screen-printed carbon surface that has lower conductivity because of the heterogeneity of the carbon ink. The Au on the SPCE had a particle-like structure. The sizes of the particles were randomly measured

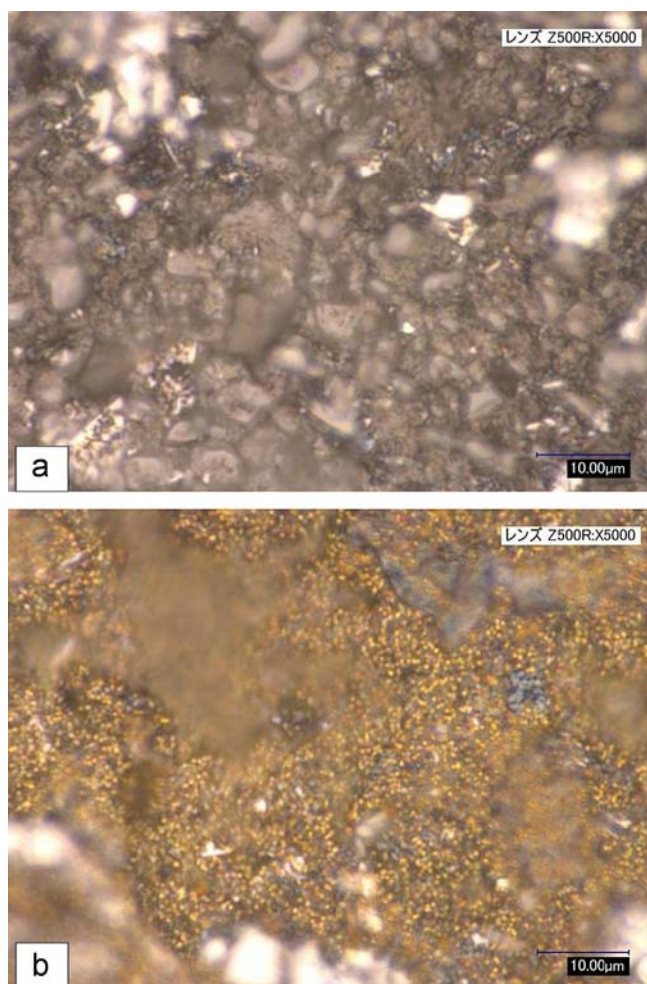


Fig. 4. Microscopic images of (a) the bare SPCE and (b) the Au-modified SPCE prepared from Table 1.

using Adobe® Photoshop® CS5 software. The mean diameter of the Au particles was 570 ± 83 nm and the number density of the particles was $\sim 0.98 \mu\text{m}^{-2}$.

3.4. The effect of the flow parameters

In the deposition step, the flow parameters that play an important role in the sensitivity of the analysis are the flow rate, deposition time and sample volume. Each of these parameters is related to the others. Therefore, the sample volume was fixed at 1.0 mL. The effect of the flow rate on the anodic stripping peak current of As was investigated over a range of $2\text{--}20 \mu\text{L s}^{-1}$ and at various deposition times. The results are summarized in Table 4. The anodic stripping peak current of As increased when the flow rates decreased. The highest peak was the peak from the procedure with the slowest flow rate of $2 \mu\text{L s}^{-1}$. However, this procedure was time consuming; the total analysis time including the cleaning step was approximately 9 min. Therefore, the optimal flow rate that gave high sensitivity and a fair analysis time was $10 \mu\text{L s}^{-1}$ (procedure D).

3.5. Analytical characteristics

A calibration graph for the determination of the As(III) concentration using SI/ASV with an Au-modified SPCE was made under the optimal conditions. The relationship was not linear;

Table 4

Procedures and results of the changes in the flow parameters with a fixed sample volume of 1.0 mL using the SI system and linear sweep anodic stripping voltammetry for the determination of As(III).

Procedure	Flow rate ($\mu\text{L s}^{-1}$)	Deposition time (s) ^a	Linear sweep anodic stripping peak current of As (μA)
A	2	520	26.87 ± 0.03
B	4	270	24.94 ± 0.13
C	6	187	21.49 ± 0.02
D	10	120	20.78 ± 0.11
E	12	100	20.40 ± 0.30
F	15	80	18.98 ± 0.14
G	20	60	17.22 ± 0.19

^a The deposition times were calculated with the additional time of the dead volume displacement.

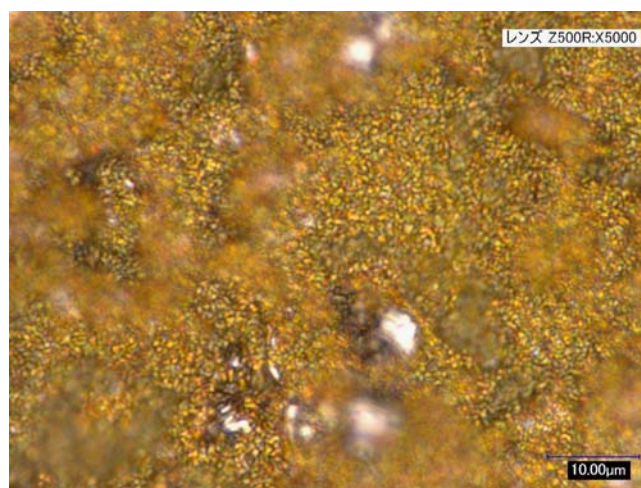


Fig. 5. Microscopic image of an Au-modified SPCE prepared by electrochemical deposition of a larger volume Au(III) solution of 9.2 mL.

the calibration was divided into two linear ranges. The linear region at the lower concentration was from 1 to $15 \mu\text{g L}^{-1}$ with a calibration slope of $0.53 \mu\text{A L } \mu\text{g}^{-1}$, and the linear region at higher concentration was from 15 to $80 \mu\text{g L}^{-1}$ with a calibration slope of $0.32 \mu\text{A L } \mu\text{g}^{-1}$. These regions are rather narrow linear ranges for As(III) detection.

To extend the linear region, the sequence for the Au modification in Table 1 was performed twice, hence, the volume of the Au(III) solution used was increased to 9.2 mL. A new calibration graph was made. The linear region has been extended to $1\text{--}100 \mu\text{g L}^{-1}$ with a calibration slope of $0.33 \mu\text{A L } \mu\text{g}^{-1}$ ($R^2 = 0.9966$). According to these results, increasing the volume of the Au(III) solution did not significantly influence the sensitivity of As detection. Microscopic images of the new Au-modified SPCE were taken (Fig. 5). The Au particles on the SPCE were larger, with a mean diameter of 685 ± 57 nm and the number density of particles also increased to $\sim 1.4 \mu\text{m}^{-2}$. We proposed that the extension of linearity is caused by the increased roughness of the Au layer on the electrode surface.

The limit of detection (LOD, the concentration corresponding to three times the standard deviation of the blank, $n = 10$) was found to be as low as $0.03 \mu\text{g L}^{-1}$ for a deposition time of 120 s and a sample volume of 1 mL. The repeatability was found from 10 measurements of a solution containing $10 \mu\text{g L}^{-1}$ of As(III) to be RSD of 1.2% and the RSD ($n = 3$) at 1 and $100 \mu\text{g L}^{-1}$ of As(III) were 8.49% and 1.72%, respectively. The reproducibility (RSD) from five different electrodes was 5.2%.

3.6. Interference study

To detect As in a real environmental sample such as ground water or surface water, several additional ions may be present. Therefore, the interference of several cations (Na^+ , Ca^{2+} , Mg^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Al^{3+} and Fe^{3+}) and some anions (Cl^- , Br^- , SO_4^{2-} , PO_4^{3-} , AcO^- , CO_3^{2-} and NO_3^-) was evaluated. Linear sweep anodic stripping voltammograms of a solution containing $10 \mu\text{g L}^{-1}$ of As(III) were recorded in the presence of each species. The interference ions were spiked and mixed together with As(III) in 1 M HCl.

The analytical results obtained from ASV can be affected by the co-deposition of metals on the electrode surface at the reduction potential used and the stripping peak of As can overlap with the stripping peak of the interferences. The interference of cations was studied at $1000 \mu\text{g L}^{-1}$ (100-fold the As(III) concentration). Regarding the considered cations, Cd^{2+} , Pb^{2+} and Cu^{2+} obviously reduced the anodic stripping peak current of As. The other cations, however, did not have an effect. Lower concentrations of each interfering cations ($100 \mu\text{g L}^{-1}$, 10-fold the As(III) concentration) were evaluated. The anodic stripping peak current of As was reduced by 0.4% and 1.3% in the presence of Cd^{2+} and Pb^{2+} , respectively, compared to the peak current without the interfering cations. Therefore, Cd^{2+} and Pb^{2+} at low concentrations do not significantly reduced the anodic stripping peak current of As. In the presence of $100 \mu\text{g L}^{-1}$ of Cu^{2+} , the anodic stripping peak current of As was also not significantly changed, but the peak potential shifted to a higher positive potential and overlapped with an anodic peak of Cu. The voltammograms are shown in Fig. 6. Therefore, out of the considered cations, only Cu^{2+} can affect the analytical measurement of As(III) detection by SI/ASV.

From the abovementioned results, the sodium ion did not affect the As(III) detection, therefore, sodium salts were chosen to study the anion interferences. Due to the possibility that environmental water is contaminated with these anions at high concentration, the anions were studied at a high concentration of 100 mg L^{-1} (10,000-fold the As(III) concentration). We found that none of the anions that were considered interfered with the anodic stripping voltammograms of the solutions containing As(III).

3.7. The removal of Cu(II) using AnaLig® TE-3

Experiments describing removal of Cu(II) using solid phase extraction (SPE) to increase the accuracy of the determination of

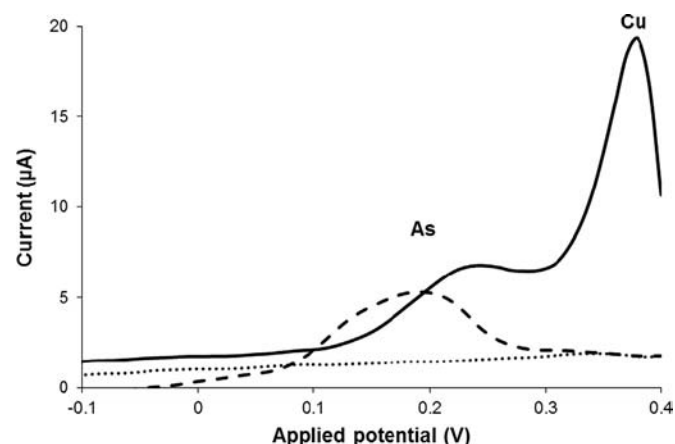


Fig. 6. A typical linear sweep anodic stripping voltammogram of a solution containing $10 \mu\text{g L}^{-1}$ As(III) in 1 M HCl and in the presence of $100 \mu\text{g L}^{-1}$ Cu^{2+} (solid line) compared to the voltammogram of a blank solution (dotted line) and the voltammogram of a solution containing $10 \mu\text{g L}^{-1}$ As(III) without interfering ions (dashed line) on an Au-modified SPCE using Au(III) solution volume of 9.2 mL.

As(III) have been reported by Furusho and collaborators [30]. Three SPE cartridges, namely, InertSep® MC-1 (cation exchange resin), InertSep® ME-1 (chelating resin) and AnaLig® TE-3 (affinity of Cu resin), were used for the elimination of Cu(II) in various solutions at pH 5, 3, 0 (1 M HCl). According to the publication, the removal of Cu(II) using MC-1 was ineffective at any attempted pH. ME-1 was effective at removing Cu(II) in solutions with pH 3 and pH 5, however the recovery of As(III) in pH 3 was inadequate. In solutions of 1 M HCl, only TE-3 was effective at removing Cu(II) with an acceptable recovery of As(III). Therefore, TE-3 was used for the removal of Cu(II) in this work because the solutions of 1 M HCl used in the extraction are suitable for direct injection into the SI/ASV for determination of the As(III) concentration.

A mixed standard solution containing $10 \mu\text{g L}^{-1}$ Cu(II) and $10 \mu\text{g L}^{-1}$ As(III) in 1 M HCl was prepared and pretreated by a manual push through an AnaLig® TE-3 cartridge (GL Sciences, Japan) using a conventional off-line SPE. Voltammograms of the mixed standard solution with and without pretreatment to remove Cu(II) using our proposed method are shown in Fig. 7. It can be observed that the anodic peak of Cu completely disappeared; therefore, TE-3 was effective for the removal of Cu(II). The recovery of As after the pretreatment by TE-3 was found to be 97% ($n=3$). In addition, TE-3 can be regenerated by eluting Cu with three bed volumes of 8 M HCl.

3.8. Application for the determination of As(III) in real water samples

The proposed method was also investigated for the determination of As(III) in real environmental water samples from a rice-field and the Chao Phraya river (Nakhonsawan Province, Thailand). The water samples were diluted with 4 M HCl (3:1 v/v) and then parted into three portions. Two portions were spiked with 11.5 and $23.0 \mu\text{g L}^{-1}$ As(III) standards. Each portion was pretreated using TE-3 cartridges for the removal of Cu(II). The pretreated samples were investigated using the proposed method with the standard calibration method. Typical voltammograms of the river water sample are shown in Fig. 8. The analytical results were obtained and summarized in Table 5. The As anodic stripping peak was not found in both of the unspiked water samples. This may be because the samples contain As concentrations less than the detection limit or that sample matrix suppresses the electrochemical response. The detection limit in real sample therefore was re-examined and found to be $0.5 \mu\text{g L}^{-1}$. The concentration of As(III)

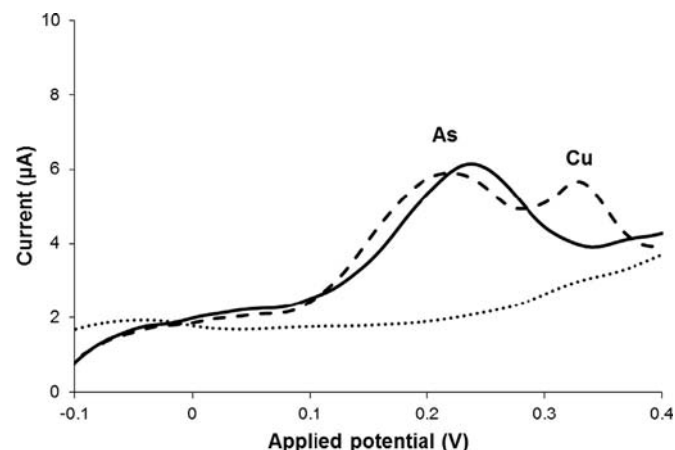


Fig. 7. Typical linear sweep anodic stripping voltammograms of a mixed standard solution containing $10 \mu\text{g L}^{-1}$ Cu(II) and $10 \mu\text{g L}^{-1}$ As(III) in 1 M HCl that was directly injected into the SI/ASV (dashed line), a solution pretreated using a TE-3 SPE cartridge (solid line) and a blank solution (dotted line) on an Au-modified SPCE using Au(III) solution volume of 9.2 mL.

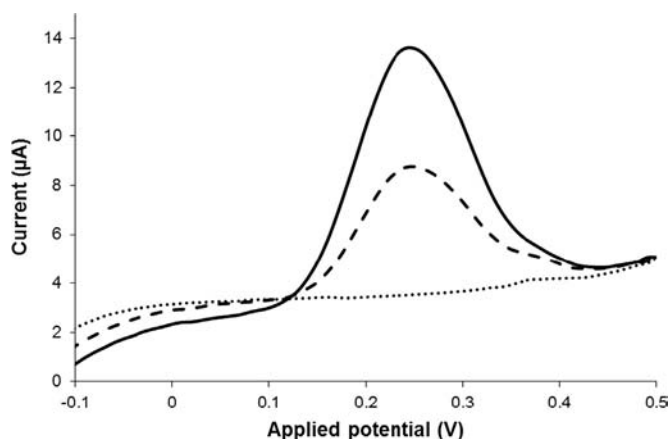


Fig. 8. Typical linear sweep anodic stripping voltammograms on an Au-modified SPCE of the pretreated river water samples (Chao Phraya river, Nakhonsawan Province) with a variation in spiked As(III) concentration; $0.00 \mu\text{g L}^{-1}$ (dotted line), $11.5 \mu\text{g L}^{-1}$ (dashed line) and $23.0 \mu\text{g L}^{-1}$ (solid line).

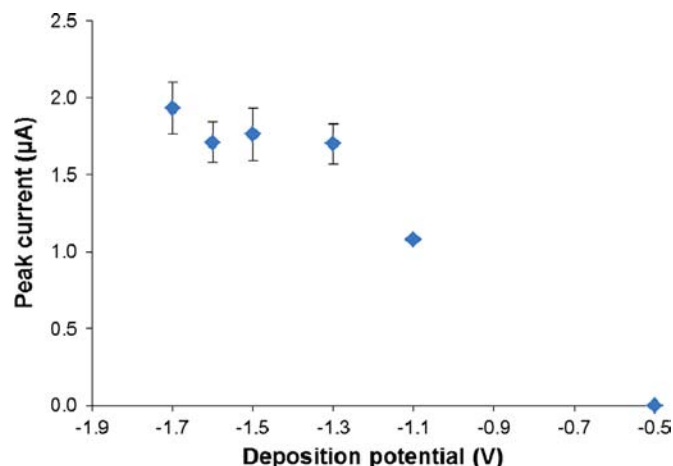


Fig. 9. The effect of the deposition potential on the As stripping peak current of solution containing $10 \mu\text{g L}^{-1}$ As(V) in 1 M HCl under the optimal conditions by SI/ASV using Au-modified SPCE.

Table 5

Determination of the As(III) concentration in real water samples using SI/ASV with an Au-modified SPCE.

Samples	Spiked As(III) concentration ($\mu\text{g L}^{-1}$)	Found As(III) concentration ($\mu\text{g L}^{-1}$)	Recovery (%)
River water	0.00	Not detected	
	11.5	12.0 ± 0.1	104
	23.0	23.4 ± 0.1	102
Rice-field water	0.00	Not detected	
	11.5	11.8 ± 0.4	103
	23.0	22.9 ± 0.1	99.5

in unspiked water samples could not be detected and the recoveries of spiked samples were found to be good in the range of 99.5–104%.

The results show that the proposed method has successfully determined the As(III) concentration in real water samples with good accuracy.

3.9. Speciation between As(III) and As(V)

In addition, the proposed method has been applied for the determination of As(V). As(V) can be reduced to As(III) with some reducing agents, such as KI, and ascorbic acid in HCl solution [31–32] or thiosulfate solution [33]. The As(III) reduced from As(V) could then be measured as the total As. However, there has been research into the determination of As(V) concentration using anodic stripping voltammetry on a boron-doped diamond electrode without using a chemical solution to reduce the As(V) [34]. A highly negative potential of -1.5 V vs. Ag/AgCl was applied in the deposition step for the direct reduction of As(V) to As(0). This was useful to our work because no additional reagents were required.

The As(V) standard solution in this work was diluted from an As_2O_5 standard solution (BHD Laboratory Supplies, England). The proposed method for the determination of As(III) was applied for the determination of As(V): the optimal deposition potential was changed. The other conditions were the same with the proposed method. The deposition potential was investigated from -1.7 to -1.1 V . The optimal deposition potential for As(III), -0.5 V , was also investigated. The results are shown in Fig. 9. A deposition potential of -1.3 V was enough for reduction of As(V). However, it is a critical point. Therefore, a deposition potential of -1.5 V vs. Ag/AgCl was chosen for the determination of As(V) concentration.

The analytical characteristics of the determination of As(V) using the optimal deposition potential of -1.5 V were also examined. The relationship between the concentration of As(V) and the anodic peak current was linear in a range of 10 – $100 \mu\text{g L}^{-1}$ with a calibration slope of $0.20 \mu\text{A L } \mu\text{g}^{-1}$ ($R^2 = 0.9964$). The detection limit was $2.3 \mu\text{g L}^{-1}$. Although the deposition potential of -1.5 V is highly negative, at which hydrogen evolution can occur. However the deposition step was carried out in a flow system which minimizes the effect of any evolved hydrogen. The repeatability of 1.0%RSD was evaluated from 10 measurements at $20 \mu\text{g L}^{-1}$ of As(V).

Furthermore, several interferences were studied for the As(V) determination and the results were similar to the As(III) determination in Section 3.6. Only Cd^{2+} , Pb^{2+} and Cu^{2+} could affect the As(V) detection. The anodic stripping peak currents of As were reduced by 3.8% and 12.5% in the presence of Cd^{2+} and Pb^{2+} at 10-fold concentrations of As(V), respectively, compared to the peak current without the interferences. The anodic stripping peak of Cu overlapped with the anodic stripping peak of As, however, Cu^{2+} can be removed out of samples by Analig® TE-3 which was reported in Section 3.7.

The speciation of As(III) and As(V) using different deposition potentials with the proposed SI/ASV method was evaluated for the determination of As(III) and As(V) in mixed standard solutions. Because of the effect of hydrogen generation at -1.5 V deposition potential, the sensitivity of As(III) determination was slightly decreased by 10%. Three calibration graphs were provided; As(III) under the deposition potential of -0.5 V , As(III) under the deposition potential of -1.5 V , and As(V) under the deposition potential of -1.5 V . The As(III) concentration was determined via the calibration equation of As(III) under -0.5 V deposition potential and then the As(III) concentration was converted to a peak current of As(III) under -1.5 V deposition potential using the calibration equation of As(III) under the deposition potential of -1.5 V . The deposition potential of -1.5 V was used to determine the concentration of total arsenic. Therefore, the concentration of As(V) can be calculated from the peak current of total arsenic subtracted by the calculated peak current of As(III) under -1.5 V deposition potential using the calibration equation of As(V). Three mixed standard solutions containing As(III) and As(V) were examined. The analytical results are shown in Table 6. The recovery efficiency of both of the arsenic species was in a good range of 95.0–104%.

Furthermore, a standard reference material (trace elements in water, SRM 1643e, National Institute of Standards and Technology, USA), which was certificated to contained $58.98 \pm 0.7 \mu\text{g L}^{-1}$ of As,

Table 6
Determination of the As(III) and As(V) concentrations in mixed standard solutions using SI/ASV with an Au-modified SPCE.

Solutions	Concentration ($\mu\text{g L}^{-1}$)					
	Spiked		Found		Recovery (%)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
No. 1	5.00	40.0	4.94 ± 0.14	38.9 ± 0.4	98.9	97.3
No. 2	10.0	30.0	10.2 ± 0.3	28.5 ± 0.6	102	95.0
No. 3	15.0	20.0	14.6 ± 0.03	20.8 ± 0.2	97.2	104

was analyzed. As(III) and As(V) concentrations in the sample was found to be 0.60 ± 0.4 and $57.7 \pm 0.4 \mu\text{g L}^{-1}$, respectively. The total arsenic was found to be $58.3 \pm 0.4 \mu\text{g L}^{-1}$. The *t*-test (significance level=0.05) indicated that there was no statistically significant difference between the determined concentration and the certified concentration.

4. Conclusions

This study is the first report to demonstrate the durability of a long-lasting Au-modified SPCE used for the determination of As concentration. The modified Au layer can be kept on the SPCE during the cleaning step by applying appropriate potential of +0.4 V vs. Ag/AgCl. At this potential, the remaining As and other metals can be oxidized and stripped away. The long-lasting Au-modified SPCE can perform voltammograms of the As(III) standard more than 300 measurements with the same sensitivity. Furthermore, if the sensitivity dropped after a long analysis about a few days, the electrode can be displaced either or renewed the Au-film through the electrodeposition. The renewed Au-modified SPCE was durable and gave as good of an analytical signal as a freshly Au-modified SPCE.

The long-lasting Au-modified SPCE was used for the determination of inorganic arsenic (As(III) and As(V)) using SI/ASV with good sensitivity and a wide linear range. The proposed method could be successfully applied to the determination of As(III) in water samples and also to the speciation of As(III) and As(V) with good accuracy.

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