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Contributed Paper

Cathodic Stripping Voltammetric Procedure for Determination of Some Inorganic Arsenic Species in Water, Soil and Ores Samples

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ABSTRACT

Square wave cathodic stripping voltammetry was developed for determination of As(III) and/or As(V) in water, soil, and ore samples. The method was based on electrodeposition of As(III) on a hanging mercury drop electrode (HMDE) as a copper-arsenic intermetallic compound, which was further reduced to arsine at a higher negative potential in the stripping step. Deposition was performed in an electrolyte solution of 1 M HCl with 10 mg L^{-1} Cu(II), by applying a constant potential of -0.40 V vs Ag/AgCl to the HMDE for 60 s at a stirring rate of 2,000 rpm. Stripping step was carried out by applying a square wave waveform in the potential range from -0.40 to -1.00 V. A voltammogram was obtained with peak potential at -0.78 V giving peak current linearly proportional to As(III) concentration up to 50 μg L^{-1}. The concentration of Cu(II) and deposition time were interrelated affecting the sensitivity of arsenic determination. With a fixed deposition time of 60 s, a narrow concentration range of Cu(II), 5-10 mg L^{-1} gave the highest sensitivity. Standard addition method was applied for quantification in order to account for effect of sample matrix. The detection limit of the method was 0.3 μg L^{-1} As(III) and the relative standard deviation for 5 μg L^{-1} As(III) (n =11) was 3.6%. As(V) concentration was determined after reduction to As(III) by using 80 mg L^{-1} of thiosulfate. The developed method was applied to the analysis of water, soil, ores leachate and ores digest samples. The results were in good agreement with those obtained by HG-AAS method and the certified value of soil certified reference material. Recoveries in range of 83-108% were obtained for water samples. The proposed method is simple, convenient, and low reagent consumption.

Keywords: cathodic stripping voltammetry, CSV; square wave, arsenic, water, soil, ores.

1. INTRODUCTION

The problems of arsenic contamination in the environment are global concerns due to its high toxicity to living organisms and its world wide distribution. Arsenic contamination in water generally comes from natural sources, through the erosion of rocks, minerals, and soils [1]. The most exposed sites of natural arsenic contamination are in Bangladesh and West Bengal, India, where arsenic levels up to 2500 μg L^{-1} in ground water have been reported [2]. Others contaminated areas include the Unites States, Taiwan, Chile, Argentina, Turkey, China, Nepal, Vietnam, and Thailand. The major cases in Thailand involve arsenic contamination of soil and water at Ron Phibun District, Nakhon Sri Thammarat province due to tin mining activities during the last century [3].

Exposure to arsenic can cause a variety of adverse health effects such as dermal changes, respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects [4]. Since 2002, U.S. EPA has lowered the maximum contaminant level (MCL) of arsenic from 50 to 10 μg L^{-1}, which is believed to be the improved level to protect human health [5]. World Health Organization (WHO) has also sets the same standard of 10 μg L^{-1} in drinking water. Toxicity of arsenic depends on its oxidation state. In natural environment, arsenic exhibits in four oxidation states: As(V), As(III), As(0), and As(-III) which are presented as inorganic and organic forms. Recently, more than 20 arsenic species of varying levels of toxicity have been identified in environmental and biological systems [6]. Inorganic arsenic species,i.e. arsenite (As(III)) and arsenate (As(V)), predominantly found in natural water, are more toxic than organic species such as monomethyl arsenic acid (MMA) and dimethylarsonic acid (DMA) which are largely found in biological samples. Arsenobetaine (AsB) and arsenocholine (AsC) widely found in seafood are non-toxic. Generally, organisms can convert toxic inorganic arsenic species to less toxic organic species.

Arsenic determination/speciation is very important and well recognized [7]. Many reviews on arsenic detection/speciation have been published [8-10]. Various techniques have been proposed for the determination of arsenic, such as spectrophotometry which is usually applied for field test kit [11], hydride generation atomic absorption spectrometry (HG-AAS) , atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), X-ray spectrometry, neutron activation analysis (NAA), electrophoresis, chemiluminescence and electrochemical techniques. Currently, well established techniques which are capable to determine several inorganic and organic arsenic species are based on chromatographic separation coupled with ICP-MS, HG-AAS, or AFS detection [12-14]. However, these methods involve sophisticated instrumentation, high operating cost and cannot be applied in the field. On the other hand, electroanalytical techniques such as stripping voltammetry [9] and stripping potentiometry [10] represent less expensive and smaller size instrumentation which could be applied to on-site analysis[15]. They are usually applied for determination of inorganic arsenic species which are very important species since arsenite is 25-60 times more toxic than arsenate and several hundred times as toxic as organic arsenicals [10].

Two approaches of stripping techniques, anodic and cathodic stripping are usually employed. Although anodic stripping is able to determine at μg L^{-1} to sub μg L^{-1} levels of arsenic, its main drawbacks are the irreproducibility due to usage of solid electrode, hydrogen evolution during deposition step and interferences from some electrochemically active ions such as copper, selenium, and mercury. Cathodic stripping voltammetry (CSV) [16-23] which usually uses hanging mercury drop electrode (HMDE) as a working electrode has better performance due to fresh electrode surface which can eliminate electrode memory effects. Electrochemical reactions involving in deposition/accumulation of As on HMDE and subsequently CSV determination have been proposed in previous studies [17,23]. Electroactive species, As(III), is electrochemically reduced to As(0), which is insoluble in Hg. However, its intermetallic compounds with Cu or Se can accumulate at mercury electrode and is further reduced to AsH_3 during the stripping step. Although the use of a mixture between Cu(II) and Se(IV) to co-deposit As(III) in CSV analysis has been reported on improving sensitivity [21], Cu(II) alone is commonly used [16-20,22,23]. Intermetallic compounds with different Cu: As ratios were formed, depending on the deposition potential and acid concentration. The following reactions were proposed for the formation of Cu-As intermetallic compounds in the deposition steps [17]:

$$H_3AsO_3 + 3H^+ + 3e^- \rightarrow As^0 + 3H_2O \qquad (1)$$

$$Cu^{2+} + Hg + 2e^- \rightarrow Cu(Hg) \qquad (2)$$

$$As^0 + 3CuCl_3^{2-} + 3e^- \rightarrow Cu_3As + 9Cl^- \qquad (3)$$

Then, in the stripping step by scanning potential of the working electrode to negative direction (cathodic scanning), the electrochemical reduction of arsenic to arsine (AsH_3) would occur:

$$Cu_3As + 3H^+ + Hg + 3e^- \rightarrow 3Cu(Hg) + AsH_3 \qquad (4)$$

During this period, a voltammogram was recorded and peak current at peak potential of about -0.8 V(vs. Ag/AgCl) was directly proportional to As(III) concentration [17,18]. The other arsenic species were determined after being converted to As(III). As(V) could be reduced to As(III) by various types of reducing agents, such as potassium iodide and ascorbic acid, sodium thiosulfate, sodium sulfite, sodium bisulfite, aqueous sulfur dioxide, hydroxylamine hydrochloride, L-cysteine and hydrazine. Table 1 summarizes the CSV methods for arsenic determination/speciation.

In this work, a simple square wave cathodic stripping voltammetric procedure was developed for the determination of As(III) and As(V) under the same condition at ppb levels using, 1 M HCl with 10 mgL^{-1} Cu(II) as a medium. It was found that lower concentration of Cu(II) provided higher sensitivity for arsenic determination than the one which have been previously reported. As(V) was determined after reduction to As(III) by using 80 mg L^{-1} thiosulfate. The higher concentration of thiosulfate as suggested in the literatures [18,22] (650 mg L^{-1}) produced colloid of sulfur which affects the sensitivity and the reproducibility for As determination. A standard addition method was used in order to accounting for matrix interferences. The proposed procedure was applied for determination of these inorganic arsenic species in water, soil, and ores samples. The method was validated using soil CRM and the results were compared with those obtained from HG-AAS.

2. MATERIALS AND METHODS

2.1 Chemicals

All chemicals used were of analytical reagent grade and ultrapure water (Milli-Q, Millipore) was used for preparing all solutions. As(III) stock standard solution (1,000 mg L^{-1}) was prepared by dissolving 0.1320 g of arsenic trioxide(Merck) with 1 mL of 25%

w/v NaOH (Lab Scan), then immediately acidified with 2 mL of conc. HCl (Carlo Erba) and adjusting to volume of 100 mL in a volumetric flask with ultrapure water. As(V) stock standard solution (1,000 mgL^{-1}) was obtained by dissolving 0.4164 g of sodium arsenate(Riedel-De Han) and adjusting volume with water in a 100 mL volumetric flask. The stock solutions were daily diluted to the concentration of 10 and 1 mgL^{-1} As. By dissolving 6.7065 g of cupric chloride dihydrate (BDH) in ultrapure water, a Cu(II) solution (10 g L^{-1}) at the volume of 100 mL was obtained. Thiosulfate solution (10 g L^{-1}, 100 mL) was prepared by dissolving 2.2134 g sodium thiosulfate heptahydrate (Fluka) in cold boiled water. Oxygen free nitrogen gas (Ultra high-purity grade, 99.9995%, Thai Industry Gas, Thailand) was used for purging solution before the analysis to remove oxygen and gaseous compounds.

2.2 Instrumentation

Cathodic stripping voltammetry was performed by using a Metrohm 757 VA Computrace Voltammograph (Metrohm, Switzerland) equipped with a voltammetric cell, a multi-mode mercury electrode, a nitrogen purge tube, and a motor-driven PTFE stirring rod. The instrument was controlled by a computer using VA Computrace software version 2.0.000 (Metrohm, Switzerland). A hanging mercury drop electrode (HMDE) working electrode, a Pt auxiliary electrode, and a Ag/AgCl/3M KCl double junction reference electrode were used.

2.3 Square wave CSV procedure

A Milli-Q water or sample solution (23.00 mL) was placed into a voltammetric cell and 2.00 mL of conc. HCl was added to obtain 1 M HCl in solution. Cu(II) solution was added to obtain 10 mg L^{-1} Cu(II) final concentration. In the case of As(V) determination, thiosulfate solution was added into the vessel to yield the final concentration of 80 mg L^{-1} thiosulfate. The same conditions of square wave CSV procedure was employed for both As(III) and As(V) determination by setting the operating parameters as follows: initial purging time: 300 s (sufficient period for complete reduction of As(V) to As(III) by thiosulfate), stirring rate: 2,000 rpm, deposition potential: -0.40 V, deposition time: 60 s, equilibration time:10 s, end potential: -1.00 V, voltage step: 2 mV, amplitude: 20 mV, frequency: 140 Hz and sweep rate: 277.8 mV. After the potential scanning, a voltammogram was recorded and peak current (μA) at the peak potential of -0.78 V was measured. Standard addition method was employed for the determination of As(III) and the total As (As(III) plus As(V)) and As(V) concentration was evaluated by subtracting total As with the As(III) concentrations.

2.4 Sample collection and preparation

Surface and well water samples from Nakhon Si Thammarat and Lampang provinces were collected in 1,000 mL polyethylene bottle. An aliquot (2 mL) of conc. HCl was added to preserve the sample. Each sample was filtered through a Whatman No. 42 filter paper immediately before the analysis.

Soil samples were collected from a gold mine in Pichit province. Samples were dried and ground to the particle size less than 180 μm after sieving. A portion (0.15 g) of the ground sample was accurately weighed and added with 10 mL of 1:1 v/v HCl, then heated until near dryness. The deigested residue was then diluted, filtered and adjusted to 100 mL with a 1% hydrochloric acid. This treatment was adequately considered to determine readily available arsenic in soil samples [24]. If total arsenic, including that

Table 1. Comparison of cathodic stripping voltammetric methods for determination/speciation of arsenic in different types of samples.

Technique	Arsenic species	Sample	Detection condition*	Reductant for As(V) reduction	Linear range (μgL^{-1})**	Detection limit (μgL^{-1})	Precision (%RSD)	Ref.
DPCSV	As(V)	sediment and water	HMDE, E_d -0.55 V, t_d 60 s,10 mV/s, ΔE 50 mV, unstir solution, 2M $NaClO_4$+0.5M mannitol+0.3M NaCl+2mM $CuSO_4$ (250 mgL^{-1} Cu(II)) pH 1.7	0.5 M D-mannitol	10-100; 0-10 (t_d 140 s)	4.4 (t_d 1 min)	5% (n=3)	16
SWCSV	As(III)	river and sea waters	HMDE, E_d -0.4 V, t_d 1-10 min, E_{step} 2 mV, ΔE 25 mV, f 70 Hz, 2M HCl, 0.8 mM $CuCl_2$ (100 mgL^{-1} Cu(II)), 0.04 mM hydrazine sulfate	-	0-42 (E_p -0.8V)	0.005 (t_d 10 min)	8% (n=11, 0.083 μgL^{-1}, t_d 1 min)	17
SWCSV	As(III) , As(V)	spring and mineral waters	As(III): HMDE, E_d -0.39 V, t_d 40 s,E_{step} 2 mV, ΔE 40 mV, f 300 Hz, stir 2000 rpm, 1M HCl, 45 mgL^{-1} Cu(II); As(V): HMDE, E_d -0.40 V, t_d 180 s,E_{step} 2 mV, ΔE 40 mV, f 300 Hz, stir 2000 rpm,1M HCl, 400 mgL^{-1} Cu(II)	3.2 mM (650 mgL^{-1}) thiosulfate	0-20 (E_p -0.82V)	As(III) 0.2 (t_d 40 s); As(V) 2.0 (t_d 180 s)	6% (n=13, 8 μgL^{-1})	18
SWCSV	As(III) , As(V)	thermal, spring and sea waters	HMDE, E_d -0.40 V, E_f -1.1V, t_d 40 s, E_{step} 2 mV, ΔE 160 mV, f 100 Hz, stir 300 rpm, 0.45M HBr, 50 mgL^{-1} Cu(II), 10 mgmL^{-1} hydrazine sulfate	3 mM sodium dithionite	0.05-0.5 ; 0-15 (E_p -0.8V)	As(III) 0.01, As(V) 0.02 (t_d 5 min)	5% (n=7, 1 μgL^{-1}, t_d 40 s)	19
CSV	As(III)	carrot, beet, irrigation water	HMDE, E_d -0.5 V, E_f -1.1V, t_d 6 min, E_{step} 5 mV, ΔE 25 mV, f 250 Hz, stir 400 rpm, 1M HCl, 150 mgL^{-1} Cu(II) + ADDTP ligand	-	0.8-12.5 (E_p -0.77 V to -0.82V)	0.5 (t_d 1 min)	5% (n=3)	20
DPCSV	As(III) ,As(V), MMA, DMA	tap, ground, sediment pore and stream waters	HMDE, E_d -0.44 V, t_d 1 min, 25 mV/s, ΔE 50 mV, stir 1000 rpm, 1M HCl, 4.6 mgL^{-1} Cu(II) + 7.4 μgL^{-1} Se(IV)	20 mM L-cysteine + 0.03 M HCl 70°C, 6 min/org. As: UV +peroxydisulfate	2.5-190 (E_p -0.68V)	0.3 (t_d 1 min)	5% (n=3)	21
DPCSV	As(III) , As(V)	natural water	copper amalgam drop electrode (Cu 211 mgmL^{-1}), E_d -0.38 V,E_f -0.86V, td 6 min, Estep 4 mV, ΔE 50 mV, stir 640 rpm, 2M HCl	3.2 mM (650 mgL^{-1}) thiosulfate	0.04-1.25 (E_p -0.68V, t_d 1 min)	0.02 (t_d 4 min)	2.5% (n=7, 0.42 μgL^{-1})	22
SWCSV	As(III), As(V)	water, soil, ore	HMDE, E_d -0.40 V, t_d 1 min, E_{step} 2 mV, ΔE 20 mV, f 140 Hz, stir 2000 rpm, 1M HCl, 10 mgL^{-1} Cu(II)	80 mg L^{-1} thiosulfate	0.3-50 (E_p -0.78V, t_d 1 min)	0.3 (t_d 1 min)	3.6% (n=11, 5 μgL^{-1}, t_d 1 min)	This work

* E_d = deposition potential, E_f = final potential, t_d = deposition time, E_{step} = step potential, ΔE = amplitude, f = frequency, rpm = round per min ** E_p = peak potential.

bound to silica, is required, a more rigorous digestion by heating with a mixture of concentrated strong acids such as hydrofluoric acid should be employed.

Ore samples were collected from lignite mines in Lampang province. Ore samples were ground to the particle size less than 180 μm after sieving. An accurately weighed of a portion (1 g) of the sample was soaked in a 100 mL pH 3 solution (adjusted by using acetic acid) for a period of 7 days. The leachate solution was obtained by filtering and adjusting to a volume of 100 mL. Ore samples (0.25 g) were digested with 10 mL hydrochloric-sulfuric acid (1:1 v/v) in a sealed Teflon vessel using a microwave oven (Perkin Elmer, USA). After cooling, samples were transferred to volumetric flask and diluted to 100 mL with a 1% hydrochloric acid.

3. RESULTS AND DISCUSSION

3.1 Optimization for As(III) determination

The principle of CSV for arsenic determination involved the reduction of electroactive As(III) in the presence of an excess of copper and/or selenium to accumulate on HMDE as intermetallic compounds which were further stripped in the cathodic scan, as previously described. As presented in Table 1, several electrolytes were proposed for CSV method for the determination of As(III) though slight improvement in sensitivity was observed. Hydrochloric acid is widely employed as a reaction medium because Cl^- can stabilize the electrogenerated Cu(I) which is required for the formation of the Cu-As intermetallic compounds (equation (3)). HBr [19] or $NaClO_4$ with NaCl [16] can also be used as a reaction medium. HCl was selected to be the supporting electrolyte in this work due to its availability and lower cost in high purity chemical grade. Cu(II) was chosen instead of Se(IV) based on the analogous reasons. It has been reported that a higher HCl concentration would result in a higher sensitivity, but baseline deterioration was found [17]. In our observation, a higher HCl concentration resulted in a higher variation in peak current of 10 μg L^{-1} As(III), i.e., relative standard deviations (n=11) of peak current when using 1 M and 2 M HCl were 3.0 and 10.9%, respectively. Therefore, the 1 M HCl was selected as a supporting electrolyte for further optimization.

The effect of deposition potential was re-investigated. Similar findings to the previous report were observed [17]. At a higher negative potential than -0.40 V, peak currents decreased due to the reduction of As to AsH_3. The deposition potential of -0.40 V was then selected for further investigation.

As it had been observed that the sensitivity for As(III) determination depended on the deposition time and Cu(II) concentration in a complex manner. This may be due to the formation of the Cu-As intermetallic compounds of different ratios [17]. For higher concentration of Cu(II), the maximum sensitivity was obtained at a shorter deposition time. Effect of Cu(II) concentration on the sensitivity of As (III) determination was investigated, at a fixed deposition time of 60 s, by considering calibration graphs (0-20 μg L^{-1} As(III)) in electrolyte solutions containing 1 M HCl with different concentrations of Cu(II). Figure 1 illustrates a plot of the slope of the calibration graph versus Cu(II) concentration. It can be seen that Cu(II) concentration is a critical parameter affecting the sensitivity (as indicated by the slope of the calibration graph) for As(III) determination. An electrolyte solution containing 5 mg L^{-1} Cu(II) provided the highest sensitivity. This should be as a result of the in-situ deposition of Cu(II) on HMDE to form intermetallic compound with As as described above, thus a suitable minimum concentration of Cu(II) was needed. However, higher concentration

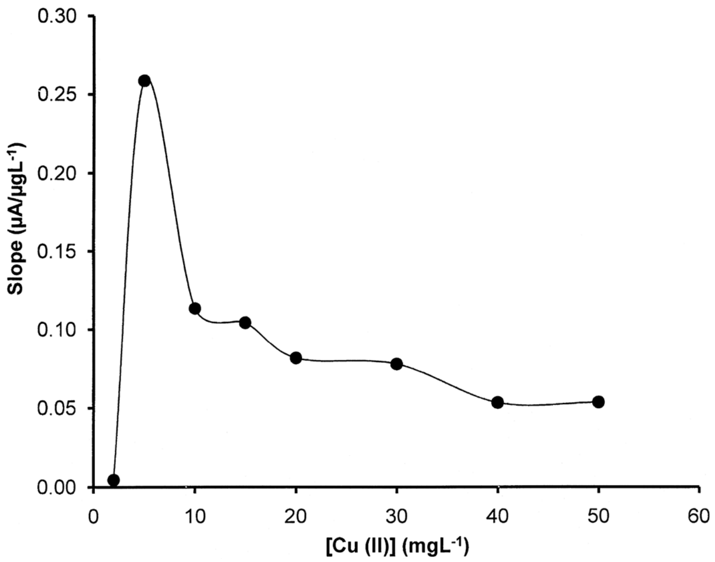

Figure 1. Effect of concentration of Cu(II) on the sensitivity of As(III) determination. (see text for conditions used).

of Cu(II) caused a decrease in sensitivity. This may be because of the formation of the intermetallic compounds of different As:Cu ratios.

By using an electrolyte solution containing 1 M HCl and 5 mg L^{-1} Cu(II), voltammograms of As(III) at the concentration range of 5-50 µg L^{-1} were recorded as shown in Figure 2. A linear calibration graph (peak current versus concentration) (y = 0.59x -2.65;

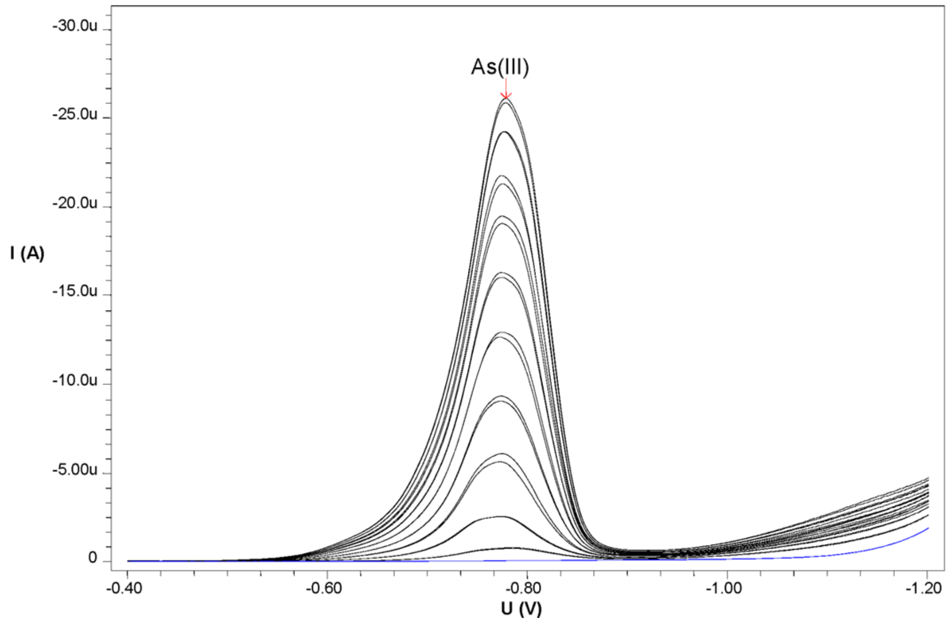

Figure 2. Cathodic stripping voltammograms of As(III) in concentration range of 5-50 µg L^{-1} (from bottom to top: 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 µg L^{-1} of As(III)). (see text for conditions used).

R^2 = 0.9935) was obtained. It was demonstrated that in the presence of Cu(II) at different concentrations led to the variation in sensitivity for the determination of As(III). Similar effects would be observed if any species, that can form complex or react with Cu(II) to alter the concentration of Cu(II) in the electrolyte solution, was present in the analyzed solution. The standard addition method should be applied for the CSV determination of As(III). This was investigated by spiking water sample with 5 mgL^{-1} of As (III) to be used as a model sample. The experiments were performed in electrolyte solutions with different concentrations of Cu(II) (5,10,15 and 20 mgL^{-1} Cu(II), as presented in Figure 3. The results indicated that only 5 and 10 mg L^{-1} of Cu(II) yielded acceptable results (for 5.0 and 4.8 mg L^{-1} As(III) found having no error and 4 % error, respectively). The more Cu(II) concentration in the electrolyte solution, the more errors were observed (about 50% and 65% errors for 15 and 20 mgL^{-1} Cu(II) as shown in Figure 3). This indicated that the sensitivity by CSV for the determination of As(III) depended on the ratio of As(III): Cu(II) in a complicate manner.

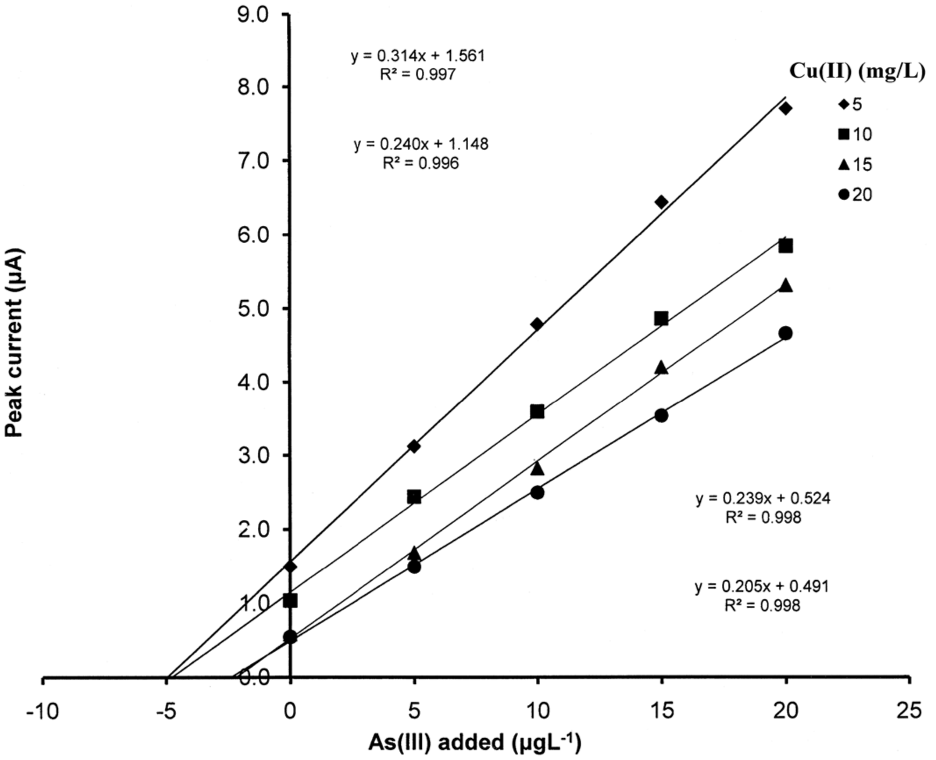

Figure 3. Standard addition graphs using different concentrations of Cu(II) for the determination of As(III) in the model water sample containing 5 µg L^{-1} As(III). (see text for conditions used).

The effect of concentration (0-100 mg L^{-1}) of Cu(II) was re-investigated for the analysis of different types of samples spiking with 30 µg L^{-1} of As(III), in order to obtain a suitable Cu(II) concentration for the analysis of real samples. The results are depicted in Figure 4. It was found that similar trends as shown in the Figure 1 were observed, but the

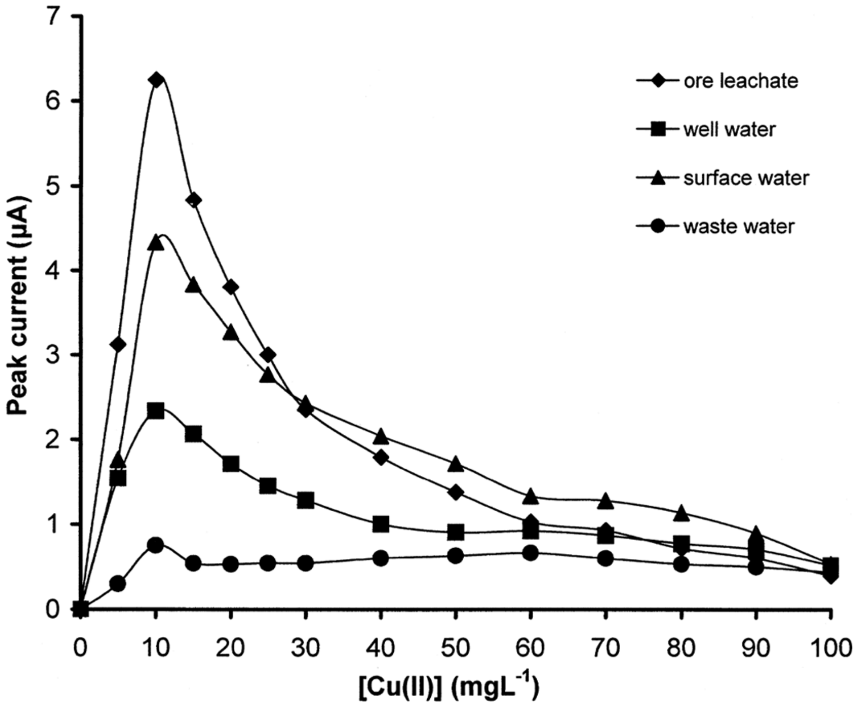

Figure 4. Effect of concentration of Cu(II) on the peak current of As(III) determination in different types of samples. (see text for conditions used).

highest sensitivity was obtained with using of 10 mg L^{-1} Cu(II). Therefore, it was chosen for the standard addition method.

The effect of stirring rate was studied in range of 400-2,500 rpm of a stirring speed. It was found that sensitivity increased with increasing of stirring rate. The stirring speed of 2,000 rpm was chosen as higher variation in peak current was observed at a higher speed.

3.2 Reduction of As(V) to As(III)

Different types of reducing agents have been used for reduction of As(V) to As(III) with different advantages and drawbacks. Several reductants are not stable, require high working temperature condition and some reductants (e.g. sulfite and hydrogen sulfite) may interfere with the As determination step, so the excess amounts of reductants have to be eliminated before the CSV step. Sodium thiosulfate was reported as a more convenient and reliable reductant which allowed rapid and complete reduction of As(V) to As(III) at room temperature without any interfering of excess amount of thiosulfate in the following As determination step [18]. Thiosulfate was chosen in this work as it is stable, readily available and easy to use. Effect of thiosulfate concentration was studied for reduction of 20 μg L^{-1} As(III) with reduction time of 300 s. Percentage reduction was obtained by comparing the peak current of the identical concentration of As(III) and that of As(V) with adding of the reducing agent. It was found that thiosulfate concentration higher than 80 mg L^{-1} should completely reduce As(V) to As(III) as shown in Figure 5. However, thiosulfate decomposed to sulfite and sulfur in acidic medium, which sulfite is dehydrated to sulfur dioxide, while the white colloid suspension of sulfur was observed at concentration of thiosulfate ≥ 90 mg L^{-1}. This colloid may affect the deposition of As on the HMDE, hence leading to the decrease in peak current of As and low reproducibility of the results. Thiosulfate at the concentration of 80 mg L^{-1} which was much lower concentration than those had been previously suggested in the literatures [18, 22] (650 mgL^{-1}), was selected as a reducing agent. By using thiosulfate at the concentration of 80 mg L^{-1}, the effect of the reduction time was studied as shown in Figure 6. The reduction time of 300 s was selected as the complete reduction of As(V) to As(III) was accom-plished. The reduction could be done during nitrogen gas purging period before voltam-metric measurement, therefore no additional time was required for the analysis.

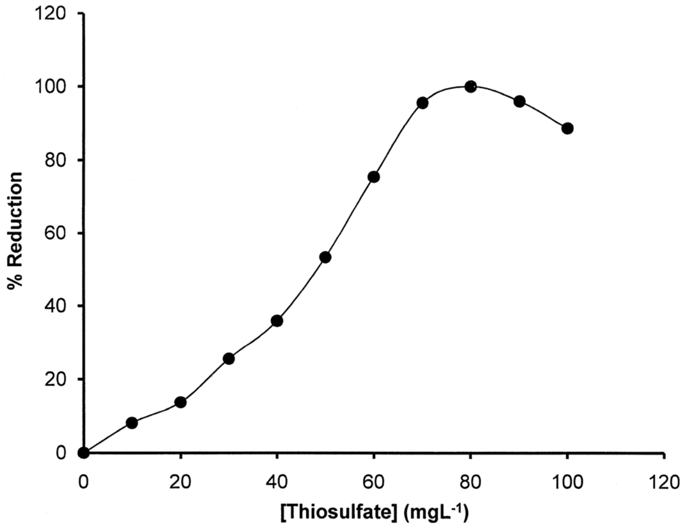

Figure 5. Effect of concentration of thiosulfate as reducing agent on reduction efficiency of As(V) to As(III) using the reducing time of 300 s. (see text for conditions used).

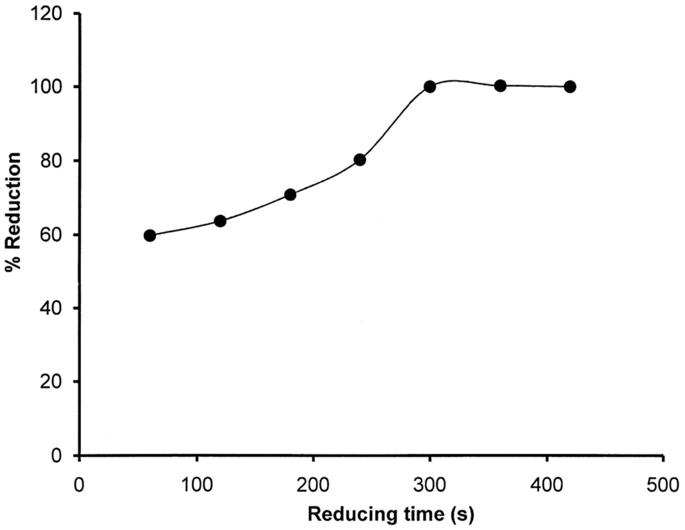

Figure 6. Effect of reducing time on reduction efficiency of As(V) to As(III) by thiosulfate at the concentration of 80 mg L^{-1}. (see text for conditions used).

3.3 Analytical features

Under the optimized conditions as described in the section 2.3, a linear response in the concentration range up to 50 mg L^{-1} with a detection limit (calculated from 3 times of the standard deviation of blank/ slope of the calibration graph) of 0.3 mgL^{-1} was obtained, which was suitable for application to various types of environmental samples. Relative standard deviation for 5 $\mu g\ L^{-1}$ As(III) (n =11) was 3.6%. The effect of sample matrix can be suppressed by using standard addition method. The proposed procedure is more convenient than the previously reported CSV methods, using the same condition for determination of As(III) and total As, after reduction of As(V) to As(III) by using thiosulfate. The analytical performances of the proposed method were compared with those of the previously reported methods as shown in Table 1.

3.4 Interferences

Interferences for the determination of As by CSV method can be classified into, firstly, metal ions that can be reduced and accumulated at the mercury electrode, which some metals can also form intermetallic compounds with As or Cu, secondly, surface active compounds that can adsorb on electrode surface, and lastly, compounds which can form complex or precipitate with As or Cu. Effects of these interferences have been investigated in literatures [16-23]. Most common ions found in natural water have been reported and these ions did not interfere [18] for the determination of As. Some interferences have been studied in this work by spiking the potential interfering ions into the solution containing 10 $\mu g\ L^{-1}$ (0.12 μM) As(III). It was found that Fe^{3+}, Cd^{2+}, Zn^{2+}, NO_2^- and NO_3^- did not interfere up to the concentration of 100 folds of As(III), whereas Sn^{2+} and Bi^{3+} at the concentration of 100 folds of As(III) caused reducing in As peak current almost half. With adding sulfide concentration at 100 folds of As, As peak disappeared at the potential of -0.78 V and a peak at more positive potential was observed (at -0.48 V). A low concentration of sulfide can be eliminated by increasing the acidity of the medium in order to transform S^{2-} to gaseous H_2S, which can be removed during purging step. Se(IV) caused the shift of the As peak to more positive potential (-0.68 V). This might be as a result of the $Se_xAs_yCu_z$ intermetallic compound formation [18].

3.5 Analysis of water, soil, ore leachate and ore digested samples

The proposed procedure was applied to the analysis of water, soil, ores leachate and ore digest, in comparison with hydride generation atomic absorption spectrophotometry (HG-AAS). Samples were prepared as described in section 2.4. The results obtained are summarized in Tables 2-4. As(III) concentration found was below the detection limit of the method in most samples. According to the reduction procedure, the total As (the combining concentration of As(III) and As(V)) was determined, and concentration of As(V) in each sample could be obtained by subtraction of the total As by the As(III) concentrations. According to paired t-test at 95% confidence level [25], the results obtained by the proposed method were not significantly different from those by HG-AAS. CRM of soil (CM PCM-6) was also analyzed. The result obtained was agreed well with the certified value.

Recoveries were studied by spiking 4 $\mu g\ L^{-1}$ of As(III) and/or 5 $\mu g\ L^{-1}$ As(V) into water samples. Percentage recoveries of 87-104 % and 83-108 % were obtained for the determination of As(III) and As(V), respectively.

Both As(III) and As(V) in $\mu g\ L^{-1}$ levels were found in surface and well water samples

Table 2. Concentration of arsenic in water samples determined by SWCSV and HG-AAS.

Sample	Concentration of arsenic found ($\mu g\ L^{-1}$)*			
	SWCSV		HG-AAS	
	As (III)	As (V)	As (III)	As (V)
Surface water**				
1	N.D.	N.D.	N.D.	N.D.
2	N.D.	N.D.	N.D.	N.D.
3	N.D.	N.D.	N.D.	N.D.
4	N.D.	N.D.	N.D.	N.D.
5	N.D.	22.9 ± 0.0	N.D.	23.2 ±0.2
6	N.D.	1.88 ± 0.02	N.D.	1.9 ±0.1
7	N.D.	N.D.	N.D.	N.D.
Well water***				
1	0.72 ± 0.09	1.57 ± 0.16	-	-
2	N.D.	2.01 ± 0.06	-	-
3	N.D.	N.D.	-	-
4	N.D.	N.D.	-	-
5	0.72 ± 0.09	1.57 ± 0.16	-	-
Surface water***	1.10 ± 0.03	6.87 ± 0.20	-	-
Tap water	N.D.	N.D.	-	-

* mean of triplicate results, N.D. = not detected, - = not analysis
** samples from Lignite mines, Lampang province
*** samples from Ron Phibun, Nakhon Sri Thammarat province

Table 3. Concentration of arsenic in soil and certified reference material of soil, determined by SWCSV.

Sample	Total As found ($mg\ kg^{-1}$)*
1	1.88 ± 0.03
2	56.7 ± 2.6
3	3.1 ± 0.1
4	33.4 ± 2.4
5	2.54 ± 0.04
6	340 ± 10
7	117 ± 3
CRM : PCM – 6**	154 ± 8

* mean triplicate results
** Certified value 162.0 ± 14.2 mg kg^{-1}

Table 4. Concentration of arsenic in ore digest and ore leachate samples, determined by SWCSV and HG-AAS.

Sample	Concentration of arsenic found (mg kg^{-1} or µg L^{-1})*			
	SWCSV		HG-AAS	
	As (III)	As (V)	As (III)	As (V)
Ores digest				
1	N.D.	30.6 ± 1.3	N.D.	31.5 ± 0.8
2	N.D.	N.D.	N.D.	N.D.
3	N.D.	N.D.	N.D.	N.D.
4	N.D.	N.D.	N.D.	N.D.
Ores leachate				
1	N.D.	N.D.	N.D.	N.D.
2	N.D.	3.2 ± 0.2	N.D.	2.9 ± 0.2
3	N.D.	1.26 ± 0.02	N.D.	1.3 ± 0.2
4	N.D.	8.4 ± 1.0	N.D.	8.6 ± 0.2
5	N.D.	N.D.	N.D.	N.D.
6	N.D.	N.D.	N.D.	N.D.
7	N.D.	1.56 ± 0.03	N.D.	1.7 ± 0.2
8	N.D.	N.D.	N.D.	N.D.
9	N.D.	N.D.	N.D.	N.D.
10	N.D.	N.D.	N.D.	N.D.
11	N.D.	N.D.	N.D.	N.D.
12	N.D.	5.3 ± 0.2	N.D.	5.7 ± 0.3

* mean of triplicate results, mg kg^{-1} for ores digest or µg L^{-1} for ores leachate, N.D. = not detected.

from arsenic contaminated site, Ron Phibun, Nakhon Sri Thammarat province, and in soil and ore samples from mining areas of the North of Thailand (Pichit and Lampang provinces). More investigations as well as arsenic remediation study should be of interest in a wider area and in various types of samples, e.g., sediment, soil, and plant [3]. The proposed method should be useful as an analytical tool for such investigation.

4. CONCLUSION

In this work, cathodic stripping voltammetry has been developed for determination of inorganic arsenic (As(III) and As(V)) in different types of sample matrices. It was found that Cu(II) which has been proposed as a metal involve in intermetallic compound formation [17,18] to increase the solubility of As in mercury electrode strongly affected on the sensitivity of As determination. A narrow concentration range (5-10 mg L^{-1}) of Cu(II) was found to provide accurate results for As determination by employing standard addition method. The developed CSV method in the present work for speciation of the inorganic As species involves the condition for reduction of As(V) to As(III) using thiosulfate solution. Thiosulfate at the concentration of 80 mg L^{-1} could completely reduce As(V) to As(III) at room temperature within 5 min, while the higher concentration of thiosulfate reduced peak current of As due to the formation of colloid/precipitate of sulfur in the solution. The proposed method was sensitive, simple, and convenient, using the same set of voltammetric conditions and chemical parameters (electrolyte solution containing 1 M HCl and 10 mg L^{-1} Cu(II)) for CSV determination of both As(III) and As(V)). The method was successfully applied for determination of the inorganic arsenic species in water, soil, ore leachate and ore digest samples.

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