Sensitive inorganic arsenic speciation on a voltammetric platform in environmental water samples

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ABSTRACT

Speciation of inorganic As using linear sweep voltammetry (LSV) on a gold (Au) working electrode was successfully carried out in environmental water samples. The linear calibration range was established from 0 to 80 μg/L As(III). The precision and accuracy of the method was tested using 50 μg/L As(III) standard solution. For precision analysis, the relative standard deviation (RSD; $N = 6$) of 5.3% was obtained for As(III) standard while for accuracy analysis, RSD ($N = 3$) was 10%. The limit of detection of the method was found to be 0.763 μg/L [As(III)]. The sensitivity of the method determined from the calibration was 224.7 nA/μM. The interference from Cu(II) was also evaluated, where its concentration up to 200 μg/L did not affect the As(III) stripping peak. The proposed method was applied for As speciation in environmental water samples from rivers around two mining regions; Gold Ridge Mine in the Solomon Islands and Sabeto in Fiji which provided reproducible and accurate results for total inorganic As, As(III) and As(V). As(III) present in the sample was first quantified using the LSV method. As(V) present in the sample was then reduced to As(III) by reaction with Na_2SO_3 and determined as total As(III) using the same method.

1. Introduction

Arsenic (As) contamination of the environment due to mining activities has been a common occurrence globally [1,2]. In addition, As toxicity to humans is well known [3]. The inorganic form of this metalloid exists as As(III) and As(V). However, As(III) is more toxic and mobile than As(V) while organic As is relatively safe [4–9]. The maximum permissible concentration of As in drinking water is 50 μg/L [1,2] and the World Health Organization (WHO) recommended value is 10 μg/L [10]. As can exert unwanted toxic effects onto life forms and thus, high levels of As in the environment is cause for concern. However, the absolute level of most metalloids in the environment like As, whilst useful does not always provide an accurate guide to toxicity. Therefore, As speciation information is required to understand its biogeochemical cycling and potential toxicity of waters [4].

Specific techniques employed to evaluate As concentrations vary [11,12]. Electrochemical analysis, particularly on a voltammetric platform such as Anodic Stripping Voltammetry (ASV), is a means of analytical measurement technique for inorganic As in the +3 and +5 oxidation states in environmental samples [6,11]. Among electrochemical techniques, ASV is a powerful tool for determining trace levels of As

(III), owing to its high sensitivity, selectivity and low detection limit [11,13,14] which arise from the pre-concentration step. The resulting voltammetric signal recorded during this process provides indication on the nature of the analyte (through the oxidation or reduction potential) and its concentration as a function of current magnitude [15,16]. Numerous studies on As determination have been carried out via ASV using various working electrode materials including Hg, Pt and Au [12], Ir, Ag and carbon based materials [15]. Among the different working electrodes, Au appears to give a more sensitive response toward As oxidation than the other electrode materials and has a higher hydrogen overvoltage than Pt [12,17–20]. The As stripping peak appears as a shoulder on the oxidation waves of Hg and Ag, and for this reason, these metals are not suitable as electrodes for As determination via ASV [12]. Thus, Au working electrode has been considered to be the most superior till date [12,17–20]. However, it has also been suggested that Au electrode should not be scanned beyond +0.7 V (versus Saturated calomel electrode) to prevent surface oxidation which could slow down the electron transfer kinetics [11].

Although ASV is a powerful technique in speciation studies, it also has drawbacks. Some of the common problems associated with ASV measurements include electrode fouling which is common in electroanalysis, interference from other metal ions and show reproducibility [21]. In ASV this effect has been minimized using cleaning steps where the working electrode can be polished and/or electrochemically cycled

to strip off fouling agents [12]. As measurements by ASV on a Au working electrode particularly suffers from Cu(II) interference in samples with high levels of this cation. Methods that can be used to counter this effect include sequestration [22], or the application of diffusion protection [23]. Dai and Compton reported that they were able to overcome this effect using Au nanoparticles (AuNPs) modified electrodes [18]. This was possible as the AuNPs were able to separate the As and Cu stripping peaks. The addition of complexing agents to the electrolyte has been also reported [24]. Thus, considering these drawbacks of ASV, the objective of the present study was to develop a linear sweep voltammetry (LSV) analytical method for the speciation of inorganic As in environmental water samples. The secondary aim of this study was to apply our developed method to evaluate the risks of As contamination in Metapona River, Solomon Islands and in the upper Sabeto River, Viti Levu, Fiji.

2. Method

2.1. Reagents

All chemicals and reagents used were of analytical grade and used without further purification. Ultrapure (Milli-Q) water, with resistivity of not exceeding 18.2 MΩ·cm, was used to prepare all solutions. Analytical grade HCl, H_2SO_4 and arsenic(III) oxide (As_2O_3) were obtained from Acros Organics (USA), while NaOH was acquired from Loba Chemie Pvt. Ltd. (India). Stock solution [1000 mg/L As(III)] was prepared by dissolving As_2O_3 powder in minimum amount of 1 M NaOH. The pH of this solution was then adjusted to 3 with 1 M HCl and the solution finally diluted to 100 mL with ultrapure water. This solution was prepared daily during As(III) detection analysis. Subsequent dilutions from the stock solution were then carried out to prepare the calibration standards in the range 0–80 μg/L. All standards were purged with N_2 gas prior to any analysis to remove oxygen.

2.2. Instrumentation, electrode pre-treatment and conditioning

Electrochemical measurements involving linear sweep stripping (LSS) voltammetry were performed using a potentiostat (eDAQ Pty Ltd., Sydney, Australia) computer controlled EChem version 2.1.15 software. A single compartment, three-electrode glass cell containing Au working electrode, a platinum (Pt) counter electrode and a Ag|AgCl reference electrode was used. All measurements were carried out at 25 °C.

Prior to the analysis, the Au electrode surface was cleaned by polishing in 0.05 μm polishing grade alumina on a fine polishing pad to a mirror finish, and washed with ultrapure water to rinse off adhering alumina particles. Then the electrode conditioning was carried out using 0.5 M H_2SO_4. Cyclic voltammetry profiles of the electrode in 0.5 M H_2SO_4 were then recorded in the potential range from 0 mV to 1500 mV (vs Ag|AgCl) at a scan rate 100 mV/s. This was repeated for 20 cycles until a stable voltammogram was achieved. This indicated the complete cleaning of the Au surface and confirmed the activation of the electrode surface [25].

2.3. Sampling sites and water sampling

Water samples were collected from eight sites along Metapona River and from five sites along Sabeto River, these are shown in Fig. 1. Polyethene sampling bottles were used for sample collection. The bottles were first cleaned with detergent and then soaked in 5% HCl for 24 h before being rinsed several times with distilled deionized water (DDW) and finally being stored in sealed plastic bags. At the sampling site, onsite filtration was carried out using a syringe filter equipped with a 0.45 μm filter. The sampling bottles were first rinsed thrice with the incoming filtered sample prior to filling. After filling, the sample was acidified to pH 2 using concentrated HCl. Nitrile disposable hand gloves were worn during sample collection. Sampling was done

in duplicates for all the sites. Physical parameters such as pH, temperature, turbidity, dissolved oxygen (DO) and salinity were also recorded for all the sites at the time of sampling. All samples were kept in ice until they reached the laboratory where they were stored in the freezer at 4 °C and analysed.

2.4. Determination of As(III) by ASV

As(III) determination in the environmental water samples was carried out using the standard addition method. For the determination of As(III), 10 mL of the filtered environmental water samples was pipetted into a vial and spiked with 200 μL of 1 mg/L As(III) standard at increasing concentration levels. Analysis was carried out in triplicates following the method reported by Dai et al. [26] with some adjustments which included an increased deposition time of 300 s and the use of a wider potential window of −344 to 500 mV for the stripping step. As(III) measurements with the Au electrode was performed via pre-concentration followed by a stripping step. Firstly, a deposition step was carried out at −344 mV (versus Ag|AgCl) for 300 s to pre-concentrate the As(III) with constant stirring using magnetic stirrer. A liner sweep voltammetric anodic (LSVA stripping step) scan was followed from −344 to 500 mV at a scan rate of 20 mV/s after which the electrode surface was electrochemically cleaned by cycling the potential at 500 mV for 30 s to ensure that all As(III) are oxidized back into the solution. At this stage, the electrode was ready for the next analysis.

2.5. Determination of total As [As(III) + As(V)]

The determination of total inorganic As was carried out by quantitative reduction As(V) to As(III) with Na_2SO_3 [27]. To a solution of 5 mL of water sample + 5 mL of 9 M HCl, 0.2 g of anhydrous Na_2SO_3 was added. The solution was then heated at 50 °C for 30 min with constant stirring. The solution was then left to cool to room temperature and then the analysis was carried out as described in this Section for the determination of As(III). The concentration of As(III) detected was the total inorganic As concentration.

3. Results and discussion

3.1. Analysis of As(III) standards and linearity

Analysis of As(III) standards was carried out using ASV in 1.0 M HCl supporting electrolyte. The As stripping peak was seen between 100 mV and 150 mV. A linear increase in current signal was observed with increasing As(III) standard concentrations from 10 to 80 μg/L which is shown in Fig. 2, with the calibration plot (inset).

Based on the calibration plot, the linear calibration range was established at 0–80 μg/L. This As(III) concentration range was used for the standard calibration plot. Spiked samples giving current signals corresponding to As(III) concentrations higher than 80 μg/L were diluted prior to analysis. From the calibration plot, the sensitivity of this method was estimated as the slope of the calibration plot, and determined as 224.7 nA/μM. A gradual decrease in sensitivity was also observed at concentrations greater than 80 μg/L. This diminished sensitivity has been previously attributed to the saturation of the Au electrode surface with the deposited As(0) which is non-conductive [28,29]. It also causes electrode fouling from As(0) and is a common problem in electrochemical analysis of As(III) at high analyte concentrations or after continuous usage of working electrode without cleaning or surface renewal [30].

3.2. Effect of interference from Cu(II)

A well-known interfering species in the detection of As(III) by ASV at Au electrodes is Cu(II) [31,32] which forms a compound with As causing the decrease of the As(III) analytical signal [17,33]. The co-deposition of Cu(II) with As(III) is well-known and results in often indiscernible peak
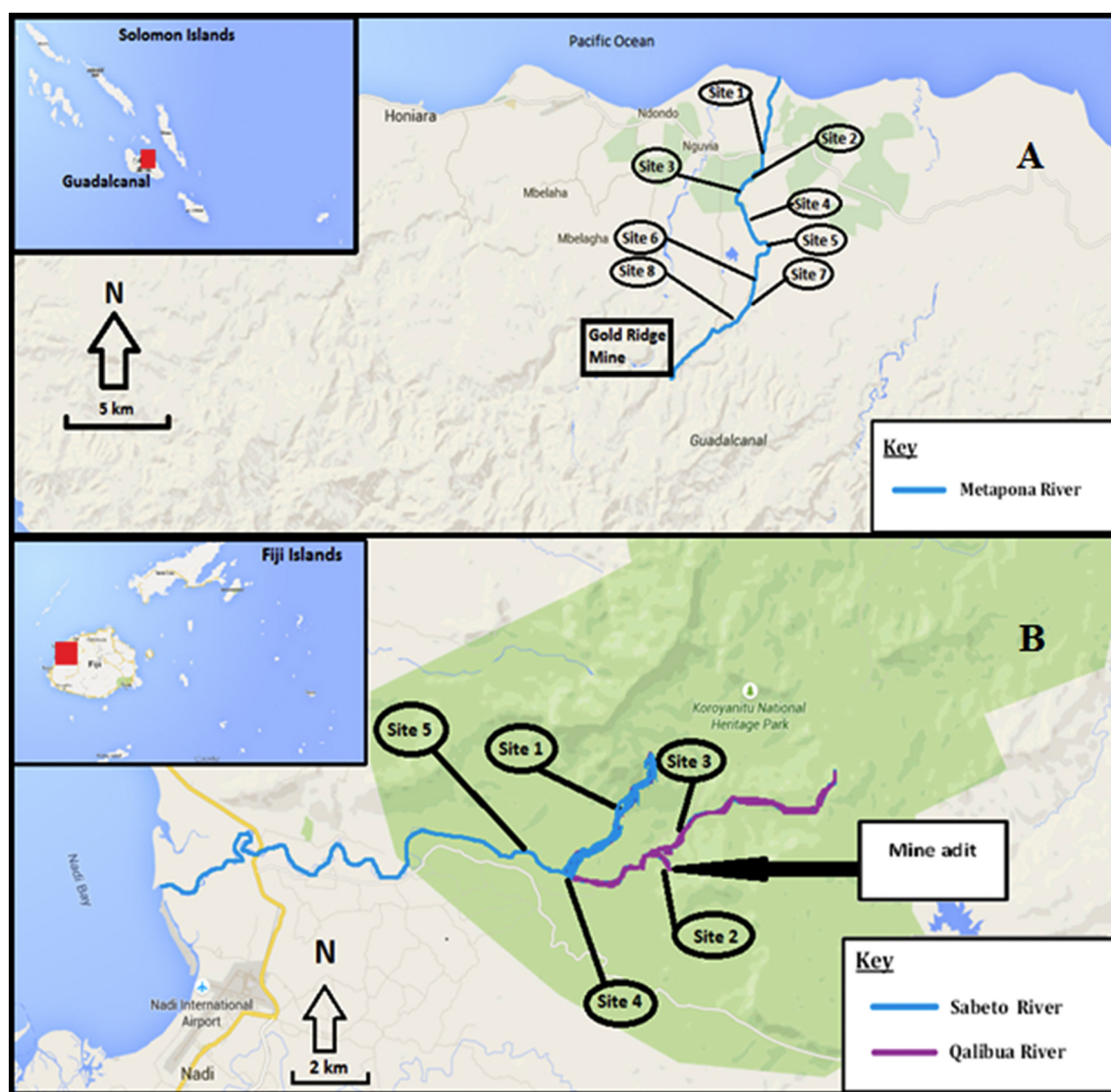
Fig. 1. Map showing location of water sampling sites along Metapona River (A) and Sabeto River (B).
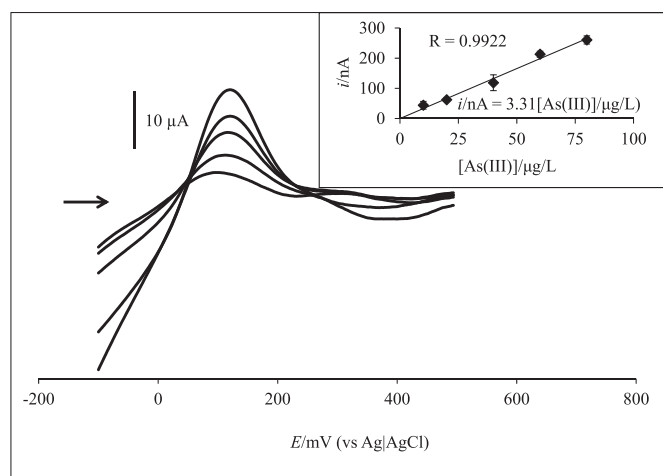(*Source*: Google maps).

Fig. 2. Linear sweep voltammetry curves of As(III) in 1 M HCl. Pre-deposition at −344 mV vs Ag|AgCl for 300 s, potential scan rate: 20 mV/s.

resolution from the stripping process of each species [34]. With high Cu (II) concentration, the stripping peak of As(III) may be partly or even totally obscured by that of Cu(II). The presence of Cu(II) has also shown to cause a positive shift in the As(III) stripping peak potential [32,35]. To evaluate this, we performed voltammetric analysis using a 50 μg/L As (III) standard in the presence of 0, 150 and 200 μg/L Cu(II) and the resulting voltammograms are shown in Fig. 3. In the presence of 0 to 200 μg/L Cu(II), the anodic stripping current of As(III) did not show any significant change. However, with the addition of Cu(II), there was a slight migration (4 mV) to a higher potential observed (from 106 mV to 110 mV) which is consistent with findings by Song and Swain [35] who have observed a positive 8 mV shift using differential pulse ASV on Au coated diamond electrodes and, attributed this to the presence of Cu(II) on the electrode. Furthermore, in the presence of 150 μg/L Cu(II), another peak started to appear at ~340 mV, which increased in height when the Cu(II) was increased to 200 μg/L. This new peak was due to the oxidation of the deposited Cu metal on the electrode surface [35] and its presence in our study is consistent with previous findings using Au electrode, which occurs around ~300–400 mV [5,32,35]. Additionally, while the As(III) and Cu(II) stripping peaks occurred at relatively close potentials, there was no effect of one on the
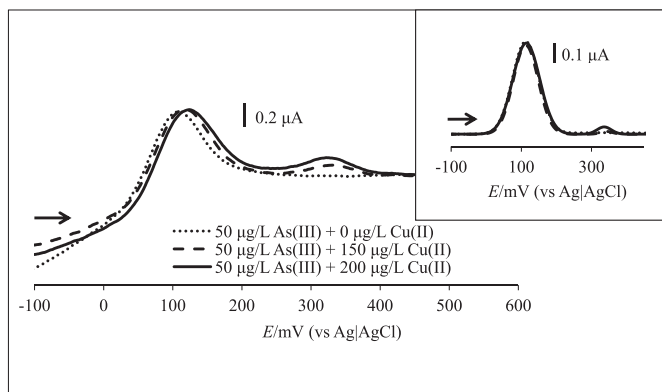
Fig. 3. Linear sweep anodic stripping voltammograms of a solution containing 50 μg/L As (III) in 1 M HCl and in the presence of 0, 150 and 200 μg/L Cu(II) respectively. Fitted voltammograms are shown inset.

other in peak integration calculations as shown in the fitted voltammograms.

3.3. As(III) and total inorganic As detection

The voltammetric responses from standard additions of As(III) to the water sample is shown in Fig. 4. Here, both fitted and unfitted results are presented although current signals were obtained from the fitted waveforms. A stripping peak seen between 100 and 200 mV in the voltammogram is due to the electrochemical stripping of As(0) to As(III) and with increasing spike volume added, the current signal showed a corresponding increase. However, at total As(III) concentrations of greater than 100 μg/L in the solution of the spiked concentration, the increase in current was attenuated which is likely due to saturation effects on the surface of the Au electrode, which coat the electrode surface with non-conducting As(0) [25,28]. It was observed that increasing As(III) concentration was accompanied by a slight increase in the background currents normally associated with the double layer charging around the electrode [16,36]. Cyclic voltammetry was performed on the spiked samples and the current signals obtained were plotted against the As (III) concentration in the sample. A 95% confidence interval associated
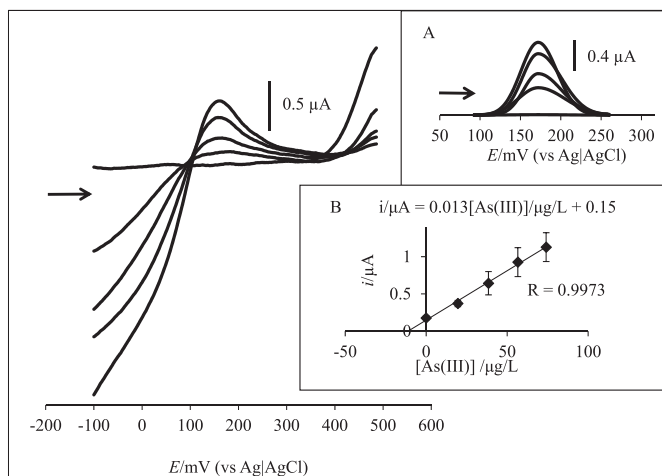
Table 1
As(III), As(V) and total inorganic As levels at each of the sites at Metapona River and Sabeto River ($N = 3$ for each site) with field parameters. Uncertainties in the [As species] show the standard deviation (SD) of the mean of three replicate measurements by ASV.

Site (S)	Mean [As (III)] (μg/L)	Mean [As (V)] (μg/L)	Mean total inorganic [As] (μg/L)	Field parameters		
				pH	DO (mg/L)	Temp. (°C)
Metapona River						
1	1.4 ± 0.1	20.3 ± 0.4	21.7 ± 0.5	7.9	6.6	28.5
2	16.3 ± 2.9	14.3 ± 1.9	30.6 ± 4.7	6.1	6.1	28.3
3	15.9 ± 0.5	10.1 ± 4.7	26.0 ± 4.2	6.4	6.2	28.5
4	5.8 ± 0.4	25.7 ± 2.6	31.5 ± 2.2	7.4	6.5	29.4
5	10.0 ± 2.2	26.0 ± 2.3	36.0 ± 2.5	7.4	6.5	30.4
6	11.9 ± 0.7	28.0 ± 1.0	39.9 ± 0.9	7.2	6.4	31.3
7	15.6 ± 0.2	22.2 ± 2.1	37.8 ± 2.2	6.6	6.3	31.0
8	20.7 ± 0.7	52.0 ± 0.9	72.7 ± 1.2	7.1	6.4	30.9
Sabeto River						
1	7.3 ± 0.8	19.5 ± 5.8	26.9 ± 5.1	7.9	8.8	20.5
2	55.2 ± 6.9	11.8 ± 2.1	67.0 ± 7.2	5.7	7.0	25.7
3	49.7 ± 1.3	14.0 ± 2.5	63.7 ± 2.8	6.2	7.3	20.1
4	30.4 ± 3.7	11.3 ± 2.5	41.6 ± 6.0	6.5	7.5	20.2
5	16.0 ± 4.5	26.9 ± 3.2	42.9 ± 5.1	7.5	7.3	21.2

with the Y-axis is also included. The concentration of As(III) in the sample was then deduced directly from the calibration graph.

The determination of total inorganic As was carried out after the reduction step which enabled the reduction of As(V) ions to As(III). Therefore, the measured concentration after this step represented all the As (III) + As(V) species i.e. the total inorganic As. As(V) concentrations were then obtained by subtracting As(III) from total inorganic As [31]. The inorganic As concentration and the field parameters in Metapona and Sabeto Rivers are shown in Table 1.

3.4. Quality control

Several quality control procedures were carried out in the analytical procedures. Firstly, all analyses were carried out in triplicates to ensure reliability of results. For each measurement the mean of triplicate determinations was presented with the respective SD.

The repeatability of the proposed method was determined using 50 μg/L As(III) standards. Six standard solutions for each concentration were prepared and analysed within one day. The RSD obtained from the repeated analysis as 5.3% was quite satisfactory to show good precision in the detection of As(III) in the water samples.

The accuracy of the method was tested by linear sweep ASV analysis 50 μg/L As(III) using standard addition technique and the respective concentration was 50.0 ± 5.0 μg/L ($N = 3$). Therefore, the accuracy of the method was considered to be quite good.

To determine the limit of detection, the procedure reported by Harris [37] was followed. Eight replicates of 5 μg/L As(III) standard were prepared and analysed. The detection limit was found to be 0.763 μg/L which is much lower than the maximum contaminant level of 10 μg/L recommended by WHO.

4. Conclusion

A gold working electrode was successfully applied for the detection and speciation of inorganic As in surface waters from rivers. The results showed that total inorganic As and As(III) levels were particularly high in both Metapona and Sabeto Rivers. For Metapona River total inorganic As concentrations ranged from 21.7 to 72.7 μg/L. Similarly, total inorganic As concentrations for Sabeto River ranged from 26.9 to 67.0 μg/L. Total inorganic As levels at both Metapona and Sabeto River were found to be at higher concentrations at Sites closer to the mine site and decreased at increasing distances from the mine.

Fig. 4. Voltammetric responses of spiked As(III) to water sample with the fitted waveforms (inset). Pre-deposition at −344 mV vs Ag|AgCl for 300 s, potential scan rate: 20 mV/s. Fitted voltammograms are shown in inset A while the Standard addition plot for the measurement of As(III) in the water sample is shown in inset B.

Acknowledgements

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