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Electrochemical co-detection of Arsenic and Selenium on a Glassy Carbon Electrode Modified with Gold Nanoparticles

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In this paper, an electrochemical sensor based on anodic stripping voltammetric technique was prepared for the co-detection (simultaneous detection) of As(III) and Se(IV) in water. A glassy carbon electrode was modified with gold nanoparticle (AuNPs) via electrodeposition by cycling from -400 mV to 1100 mV and used as the substrate. The presence of AuNP on the electrode enhanced both the stripping current and peak resolution for both arsenic and selenium. The deposition potential, pH and choice of electrolytes were optimised. A detection limit of 0.15 ppb (As(III)) and 0.22 ppb (Se(IV)) was obtained with good reproducibility. The method was applied to real water sample and validated with inductively coupled plasma – optical emission spectroscopy.

Keywords: arsenic; selenium; gold nanoparticle; electrochemical co-detection; anodic stripping voltammetry

1. INTRODUCTION

Selenium is known as one of the essential nutrients for human health with a narrow range between essentiality and toxicity [1]. It is a component of different types of proteins that perform vital functions in the body. However, when selenium is not sufficient in the body it can lead to health challenges such as cardiovascular disease, liver and heart disease, loss of hair, low immunity, constant tiredness, mental retardation and reproductive abnormality [2]. When selenium is taken in excessive quantity it can also cause health related problems which include nerve damage, gastro intestinal disturbance, nausea, vomiting and sore of the skin [2-3].

In the environment, selenium can be found in different oxidation states which are (+VI, +IV, 0 and -II), among all these oxidation states, the +IV oxidation state of selenium is the only oxidation state of selenium that is electroactive and most toxic [4].

Arsenic has been documented to be one of the most harmful elements on the earth surface, often times, human being get contacted with arsenic through water, air and food [5]. Interestingly, arsenic and selenium have four oxidation states, but the oxidation states of arsenic are (+V, +III, 0 and –III) under different redox reactions [6]. Arsenic is majorly present as trivalent arsenite As(III) and pentavalent arsenate which is As(V) in natural water. It has been documented that the +III oxidation state of arsenic is more harmful than its +V oxidation state [7].

The toxicity of arsenic and selenium has made World Health Organisation to set a permissible limit of 10 μgL^{-1} for arsenic and selenium concentrations in drinking water [2,8]. The detrimental effects of arsenic and selenium lead to health complications generally known as arsenicosis and selenosis [9].

Owing to the environmental importance of selenium and the toxicity of arsenic and selenium, their detections and quantifications have been investigated using different methodologies. To date, different analytical methods have been used by scientists and analytical chemist to detect arsenic and selenium. Although spectroscopy and inductively coupled plasma methods have been successfully used for the detection of As(III) and Se(IV), yet the major challenges associated with these methods are the following: instruments are very expensive, high cost of operation, laboratory setup, the time for analysis is relatively high, it requires highly trained personnel, the instruments are not portable and this makes it difficult to be utilized on site [10]. For instance, graphite furnace atomic absorption spectroscopy [11-12], hydride generation atomic absorption spectroscopy [13-14] and atomic fluorescence spectrometry [15-16] have been explored for the detection of arsenic and selenium. One of the suitable alternatives with characteristic that meet the challenges highlighted, are electrochemical techniques (particularly stripping voltammetry) which have been explored for different metal detections. Electrochemical methods have been shown to possess some advantages such as portability of the instruments, excellent sensitivity to trace metals in ppb range, affordable price and fast analysis time [17-19]. Anodic stripping voltammetry (ASV) have been explored for the detection of different metals and semi metals such as Pb [20-21], Hg [21-22], Cd [23-24], Se [17][25-26] and As [27-28] to name a few. ASV technique has the ability to detect metals at different oxidation states with detection limits in the sub ppb concentrations [29-30].

Different types of electrodes such as Hg [31], Pt [32- 33] and Au [34-37]. have been utilised in anodic stripping voltammetry. The use of gold electrodes presents an added advantage over other electrode types in its ability to form Au-As intermetallic alloy/compounds which can enhance the detection of As especially during the cathodic pre-concentration step [38- 39]. The use of gold in the nanoparticle size regime is expected to possess added advantages over the use of bulk gold owing to the markedly increased surface area of nanogold. This potential has been exploited in the literature where gold nanoparticles (AuNPs) have been used for the anodic stripping voltammetry analysis of As(III) solution [40-42]. In this work we have demonstrated a simple electrodeposition of nanogold without any additional modifier for the co-detection of arsenic and selenium. This work is a step ahead of our previous report where selenium only was electrochemically analysed on a AuNPs modified glassy cabon electrode [17].

2. EXPERIMENTAL

2.1 Material and methods

As_2O_3, Na_2SeO_3, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $CaSO_4$, $MgSO_4$, $HAuCl_4$ and HCl were bought from sigma Aldrich. All chemicals used for these experiments are used as obtained and were all prepared in deionised water. All electrochemical experiments were done on an Ivium Compactstat potentiostat (Netherlands). The instrument is attached to three electrode systems which are counter electrode (CE), working electrode (WE) and reference electrode (RE). The counter electrode is platinum wire; glassy carbon electrode was used as working electrode and Ag/AgCl (3M KCl) as reference electrode. The electrochemical cells were de-gassed with ultra-pure argon gas for 10 minutes before carrying out any electrochemical measurements. Inductively coupled plasma – optical emission spectroscopy (ICP-OES) technique was carried out on iCAP 6000 ICP spectrometer instrument Thermo Fisher Scientific (USA) and was used to validate the electrochemical result for real water sample experiment.

2.2. Electrode modification

The modification of GCE by AuNPs was carried out by electrodeposition using cyclic voltammetry (CV) of potential range from -400 mV to 1100 mV for 10 cycles at a scan rate of 50 mV s^{-1}. This method has been shown to yield gold of nanoparticle size on the surfaces of electrodes [43]. The glassy carbon electrode modified with gold nanoparticles was ascribed as GCE-AuNPs and characterised by using EIS in the presence of 1 mM $[Fe(CN)_6]^{3-/4-}$ in which 0.1 M KCl was used as supporting electrolyte.

2.3. Co-detection of arsenic and selenium

Square wave anodic stripping voltammetry (SWASV) was used for the co- detection of As(III) and Se(IV) in water using GCE-AuNPs as the working electrode. The optimisation conditions for the experiment include electrodeposition potential of -500 mV, deposition time of 30 s and a 0.1 M H_2SO_4 as the supporting electrolyte. Square wave voltammetry (SWV) measurements were recorded at potentials ranging between -1200 mV to 1500 mV to accommodate the stripping of As and Se. The modified electrode was subjected to a potential of 1200 mV for 90 s to remove excess As(III) and Se(IV), followed by a SWV sweep in solution that does not contain As(III) and Se(IV). For real water analysis, a 0.2% (v/v) nitric acid was added to the real water sample before analysis on the ICP-OES to aid digestion and same procedure was also carried out on the real sample analysis for electrochemical method.

3. RESULTS AND DISCUSSION

3.1 Electrochemical characterisation

The bare and GCE-AuNPs were characterised with electrochemical impedance spectroscopy (EIS) in 1 mM [Fe (CN) $_6$]$^{3-/4-}$ redox probe as depicted in Fig. 1. EIS is an electrochemical technique suitable for the interrogation of interfacial electron transfer as a result of changes at the electrode surface when modified [44]. The semi-circle diameter at higher frequencies connotes the electron transfer resistance (R_{ct}) and the linear part at lower frequencies connotes the diffusion process. A well-defined semi-circle was displayed by the bare GCE at higher frequency, the semicircle diameter reduced markedly (reduction in charge transfer resistant R_{ct}) when AuNPs were used to modify the GCE (Fig. 1), implying that AuNPs are excellent electric conducting materials and they can accelerate electron transfer.

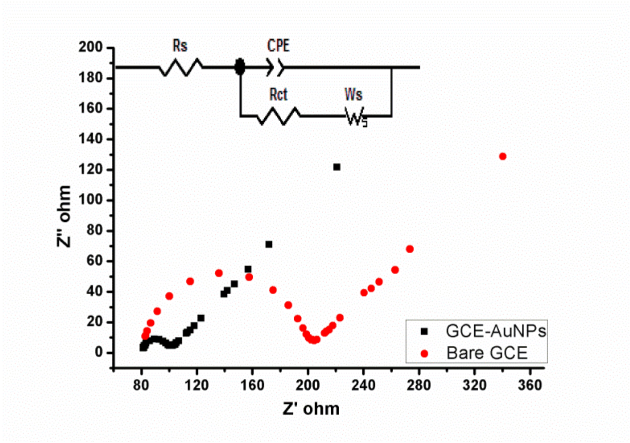


Figure 1. EIS of bare GCE and GCE-AuNPs in 1 mM [Fe(CN)$_6$]$^{3-/4-}$ redox probe. The EIS measurement was carried out using 0.1 Hz to 100 kHz, alternate voltage of 5 mV and bias potential of 0.22 V.

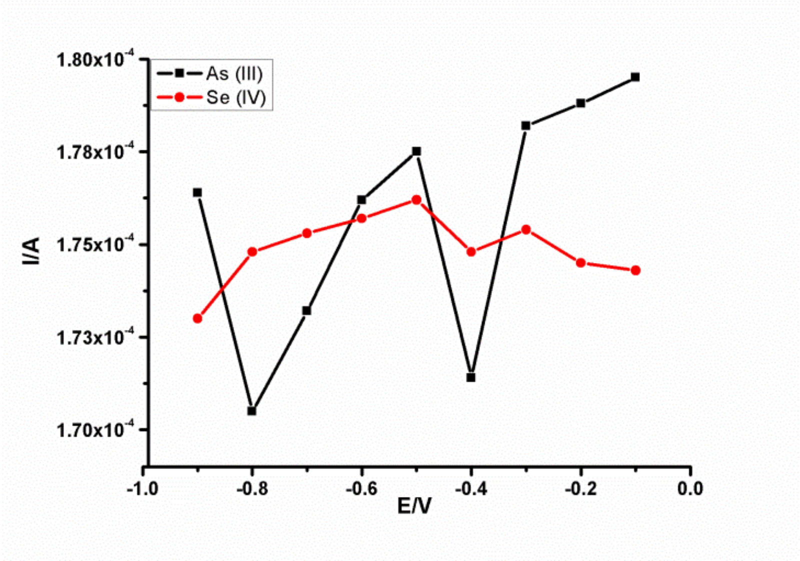
3.2 Effect of deposition potential, deposition time, pH and supporting electrolyte on co-detection of Arsenic and selenium

The effect of electrodeposition potential (varied from -100 mV to -900 mV) was studied during the co-detection of arsenic and selenium. The result (Fig. 2a) for As(III) showed a decrease in peak from -0.1 mV to -0.4 mV but was increased at -0.5 mV and started decreasing from –0.6 mV to -0.8 mV. Although, -0.1 mV gave the highest peak current for As(III) and lower peak current for Se(IV), -0.5 mV was used as the optimisation potential for the co-detection of As(III) and Se(IV).

The pre-concentration time was varied from 30 s to 360 s. The results **(**Fig. 2b**)** showed a decrease in current with an increasing deposition time from 30 s to 360 s for both analytes. Hence, electrodeposition time of 30 s while stirring was used as optimum condition for all electrochemical experiments of arsenic and selenium. Adeloju et al also used electrodeposition of 30 s as the optimisation time to determine arsenic on a mercury film electrode in the presence of copper (II) ions [42].

The electrochemical response of As and Se stripping at different pH was investigated and presented in Fig. 2c. It is important to carry out pH studies experiment because the ionic states of our analytes are influenced by the proton environment in which they exist. Since pH 1 gave the best peak current signal it was utilized for all subsequent experiments. A similar pH for As stripping has been reported by Compton et al [43].

The electrochemical response of supporting electrolyte is shown in Fig. 2d. At neutral supporting electrolyte, no visible peaks of the analytes were observed, but acidic supporting electrolytes gave clear peaks of the two analytes. In this work, 0.1 M H_2SO_4 was selected as the supporting electrolyte since it produced the highest current signal for the stripping of As(III) and Se(IV) in support of other reports in literature [17, 44]. These experimentally optimised parameters further used for electroanalysis.



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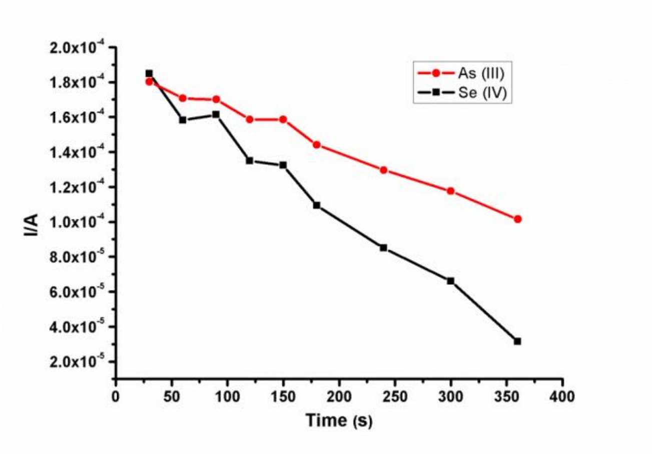

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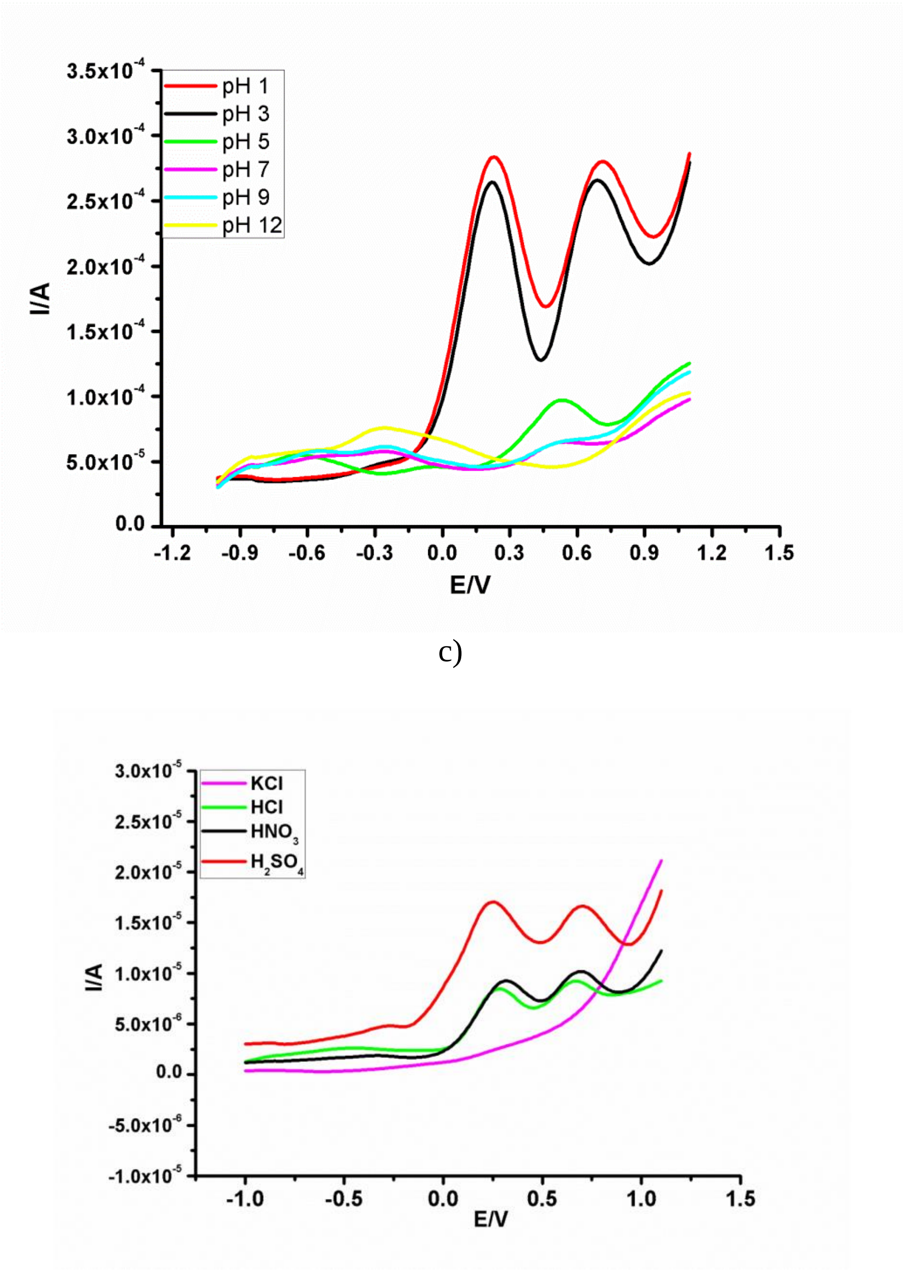


c)

d)

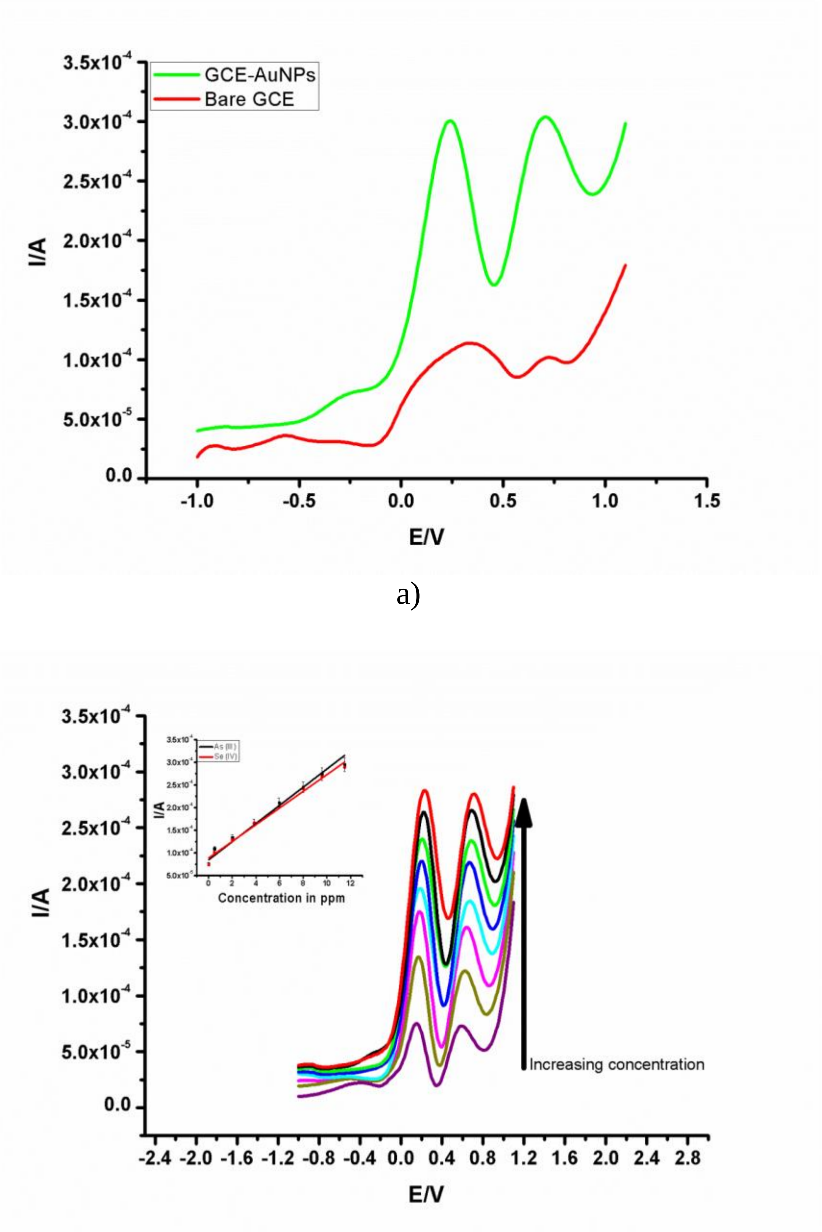
Figure 2. (a) Effect of different electrodeposition potentials on 2 ppm [As(III) and Se(IV)] solutions (b) Effect of electrodeposition time on 2 ppm [As(III) and Se(IV)] solutions (c) Effect of 12 ppm [As(III) and Se(IV)] solutions on different pH (d) Effect of different supporting electrolytes evaluated on 500 ppb [As(III) and Se(IV)] solutions.

3.3 Co-detection of Arsenic and Selenium

GCE-AuNPs electrodes show enhance peak current signal than bare GCE as depicted in Fig. 3a. This marked current amplification of As and Se was due to the fact that gold nanoparticles increase the surface area and also facilitate the electron transfer of the analytes to the electrode surface.

Square wave voltammetry of different concentrations between 0.01 -12 ppm were examined and the peak currents were found to be directly proportional to the concentration of arsenic and selenium

(Fig. 3b). The linear regression equation for As(III) detection was y= 2.0666×10^{-5} x + 8.4668×10^{-5} and for Se(IV) detection y= 1.8428×10^{-5} x + 8.8673×10^{-5} with R^2 value of As =0.9854 and 0.9877 for Se(IV). The detection limit was calculated from this equation $C_L=3S_B/m$[42]. C_L, S_B and m connote the limit of detection, standard deviation of the blank and the slope of the calibration graph was calculated to be 0.15 ppb (As(III)) and 0.22 ppb (Se(IV)).



a)

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Figure 3. (a) SWASV of 12 ppm [As(III) and Se(IV)] solutions on bare GCE and GCE-AuNPs. (b) SWASV of GCE-AuNPs for co-detection of As(III) and Se(IV) within a range of 0.01-12 ppm in 0.1 M H_2SO_4 as supporting electrolyte (pH 1) and deposition time of 30 s. Potential vs Ag/AgCl (3 M KCl).

The experiments were carried out in triplicates with good reproducibility and relative standard deviation (RSD) of 2.8% and 3.2% for As(III) and Se(IV) respectively. The detection limits obtained from both analytes showed that the reported electrochemical sensor has analytical significant and thus has potential for environmental samples. This detection limit of this sensor compares well with those reported in the literature (Table 1). Furthermore, we report a wider liner linear range (Table 1). Although gold nanoparticles have been used as a modifier for the electroanalysis of selenium, we were able to use this modifier for simultaneous detection of arsenic and selenium. The detection limits obtained for both analytes were far below the acceptable limit by World Health Organisation [4, 49].

Table 1. Comparison of the detection limits of some reports on the electrochemical detection of As(III) and Se(IV)

Electrode used	Technique	Linear Range	Detection limit	Analyte	Reference
Au-Cu bimetallic nanoparticles	SWASV	20-200 ppb	2.09 ppb	As	[27]
Cobalt oxide nanoparticles	CV	10-50 ppb	0.11 ppb	As	[45]
Disc gold electrode	DPASV	0.2-250 ppb	0.15 ppb	As	[46]
GCE-AuNPs	SWASV	0.001-50 ppm	0.34 ppb	Se	[17]
GCE-Bismuth Film	DPASV	2-30 ppb	0.1 ppb	Se	[47]
Micro fabricated gold	SWASV	100-500 ppb	0.42 ppb	Se	[48]
GCE-AuNPs	SWASV	0.01-12 ppm	0.15 ppb	As	This work
GCE-AuNPs	SWASV	0.01-12 ppm	0.22 ppb	Se	This work

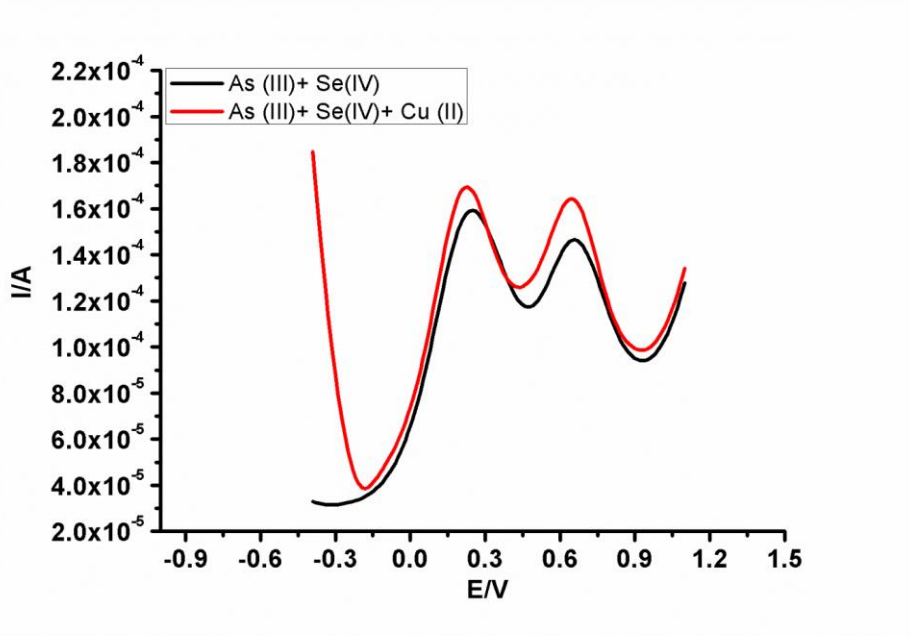
SWASV-Square Wave Anodic Stripping Voltammetry, CV- Cyclic Voltammetry, DPASV-Differential Pulse Anodic Stripping Voltammetry, LOD- Limit of Detection

3.4 Experimental report on Interference studies and real water analysis

The GCE-AuNPs sensor was not affected by some cations such as $Mg^{2+,}$ $Ca^{2+,}$ Na^{+} and K^{+}. However, minimal interference was observed from Cu^{2+} and Cd^{2+} as depicted in Fig 4a and b. On adding equal concentrations of copper to arsenic and selenium sensing, there was about 6.25% peak enhancement of As and Se peaks as depicted in Fig 4a, this enhancement could be due to the formation of alloys such as As-Cu-Se during the electrodeposition step, which may enhance the peak current signal. In the same vein, equal concentration of cadmium was added to arsenic and selenium sensing, there was about 2.3% decrease in peak of As and Se peaks as depicted in Fig 4b, this slight decrease could also be as a result of formation of alloy which is As-Cd-Se during the electrodeposition step.

The suitability of the developed sensor for environmental applications was tested with real water sample from the effluent of one of the industries in South Africa (Fig 4c). A 0.2% (v/v) nitric acid was added to the real water sample before analysis on the ICP-OES to aid digestion; same procedure was also carried out on the real water sample analysis for electrochemical method.

A concentration of 5.23 (± 0.42) ppb As(III) and 5.16 (±0.75) ppb Se(IV) were calculated for the real water sample (n=3) as depicted by Fig 4c. For comparison, ICP-OES analysis at n=3 gave 5.60 (±0.22) ppb As(III) and 3.7 (±0.75) ppb Se(IV). Using t test at 95% confidence level, the value of $t_{observed}$ (2.26) was less than $t_{critical}$ (2.74) for As(III) and value of $t_{observed}$ (2.17) was less than $t_{critical}$ (2.65) for Se(IV). This result shows an agreement with variations due to random error, thus a validation of the reported method. The concentrations of the two analytes in the real water samples are within the acceptable limit of 10 ppb as documented by World Health Organisation [2, 8].



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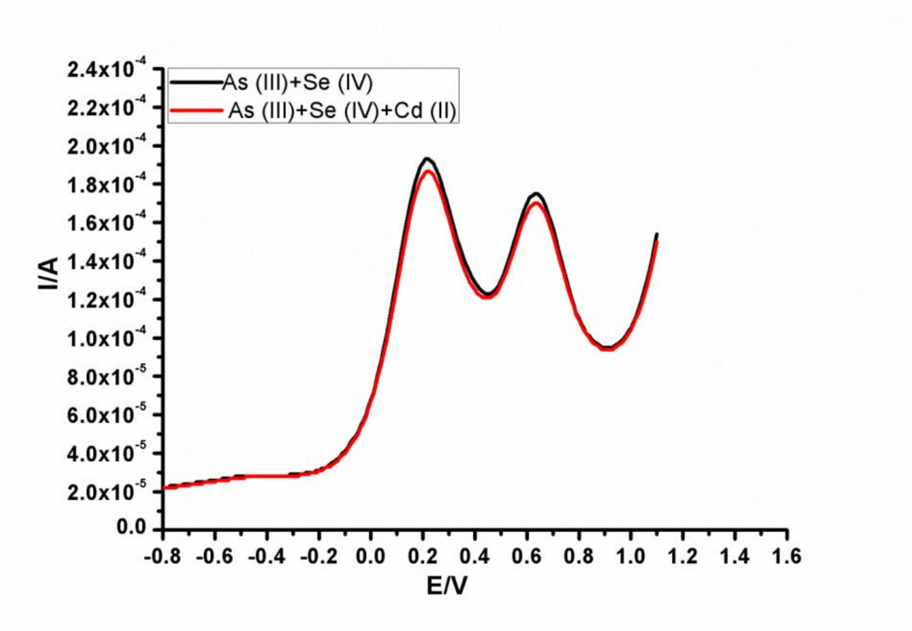

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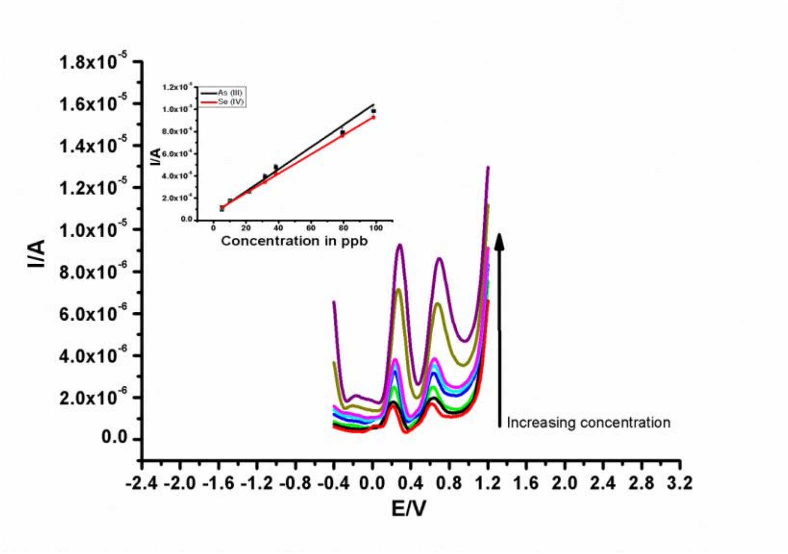

c)

Figure 4. a) SWASV of 1000 ppb solutions of [As(III) and Se(IV)] + 1000 ppb Cu^{2+} on GCE-AuNPs. b) SWASV of 2000 ppb solutions of [As(III) and Se(IV)] + 2000 ppb Cd^{2+} on GCE-AuNPs. c) SWASV of co-detection of [As(III) and Se(IV)] in real water sample with calibration plot (inset).

4. CONCLUSION

In this work, GCE-AuNPs was satisfactorily utilised for the first time as an electrochemical sensor to co-detect arsenic and selenium with very low detection limits. GCE-AuNPs demonstrated good reproducibility. There was good correlation with results obtained from ICP-OES and thus validating this method. Thus showing the analytical significant of our sensor.

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References

1. S. M. Hays, K. Macey, A. Nong and L. L. Aylward, *Regul. Toxicol. Pharmacol.*, 70 (2014) 339.
2. M. R. Awual, T. Yaita, S. Suzuki and H. Shiwaku, *J. Hazard. Mater.*, 291 (2015) 119.
3. H. J. Sun, B. Rathinasabapathi, B. Wu, J. Luo, L. Pu and L.Q. Ma, *Environ. Int.*, 69 (2014) 158.
4. V. Beni, G. Collins and D.W.M. Arrigan, *Anal. Chim. Acta*, 699 (2011) 133.
5. Y. Liu and W. Wei, *J. Electroanal. Chem.*, 624 (2008) 304.
6. J. F. Huang and H. H. Chen, *Talanta*, 116 (2013) 859.
7. J. Theytaz, T. Braschler, H. Van Lintel, P. Renaud, E. Diesel, D. Merulla and J. Van der Meer, *Procedia Chem.*, 1 (2009) 1006.

8. M. M. Karim, *Water Res.*, 34 (2000) 310.
9. J. E. Spallholz, L. M. Boylan and M. M. Rhaman, *Sci. Total Environ.*, 323 (2004) 32.
10. Q. Hu, L. Li, Y. Wang, H. Zhao and G. Zhuang, *J. Environ. Sci.,* 22 (2010) 1474.
11. J. Y. Cabon and N. Cabon, *Anal. Chim. Acta,* 418 (2000) 31.
12. S. Xu, M. Zheng, X. Zhang, J. Zhang and Y. I. Lee, *Microchem. J.*, 101 (2012) 74.
13. O. Duben, J. Boušek, J. Dědina and J. Kratzer, *Spectrochim. Acta, Part B At. Spectrosc.,* 111 (2015) 63.
14. K. Anezaki, I. Nukatsuka and K. Ohzeki, *Anal. Sci.*, 15 (1999) 834.
15. S. Afton, K. Kubachka, B. Catron and J. A. Caruso, *J. Chromatogr., A* 1208 (2008) 163.
16. Z. G. Liu, X. Chen, J. H. Liu and X. J. Huang, *J. Hazard. Mater.*, 278 (2014) 74.
17. A. O. Idris, N. Mabuba and O. A. Arotiba, *J. Electroanal. Chem.*, 758 (2015) 11.
18. P. J. Mafa, A. O. Idris, N. Mabuba and O. A. Arotiba, *Talanta,* 153 (2016) 106.
19. I. Rutyna and M. Korolczuk, *Sensors Actuators B Chem.,* 204 (2014) 141.
20. T. Ndlovu, O. A. Arotiba, S. Sampath, R. W. Krause and B. B. Mamba, *J. Appl. Electrochem.*, 41 (2011) 1396.
21. M. Zaib, M. M. Athar, A. Saeed and U. Farooq, *Biosens. Bioelectron.*, 74 (2015) 908.
22. M. P. N. Bui, J. Brockgreitens, S. Ahmed and A. Abbas, *Biosens. Bioelectron.,* 85 (2016) 286.
23. G. Zhao, H. Wang, G. Liu and Z. Wang, *Sensors Actuators B Chem.*, 235 (2016) 73.
24. G. Bhanjana, N. Dilbaghi, R. Kumar, A. Umar and S. Kumar, *Electrochim. Acta*, 169 (2015) 102.
25. D. W. Bryce, A. Izquierdo and M. D. L. De Castro, *Anal. Chim. Acta,* 308 (1995) 101.
26. C. F. Pereira, F. Gonzaga, A. Guaritasantos and J. Souzade, *Talanta*, 69 (2006) 881.
27. M. Yang, G. Zheng, L. Li, Y. Huang, J. Liu, Q. Zhou, X. Chen and X. Huang, *Sensors Actuators, B Chem.*, 231 (2016) 78.
28. T. Ndlovu, B. B. Mamba, S. Sampath, R. W. Krause and O. A. Arotiba, *Electrochim. Acta*, 128 (2014) 53.
29. T. Ndlovu, O. A. Arotiba, S. Sampath, R. W. Krause and B. B. Mamba, *Phys. Chem. Earth, Parts A/B/C* 50-52 (2012) 131.
30. B. C. Janegitz, L. H. Marcolino-Junior, S. P. Campana-Filho, R. C. Faria and O. Fatibello-Filho, *Sensors Actuators B Chem.*, 142 (2009) 266.
31. S. B. Adeloju, T. M. Young, D. Jagner and G. E . Batley, *Anal. Chim. Acta*, 381 (1999) 213.
32. Z. Wei and P. Somasundaran, *J. Appl. Electrochem.,* 34 (2004) 244.
33. J. Lee, D. W. M. Arrigan and D. S. Silvester, *Sens. Bio-Sensing Res.*, 9 (2016) 44.
34. G. Elumalai, H. Noguchi, A. Lyalin, T. Taketsugu and K. Uosaki, *Electrochem. commun.,* 66 (2016) 57.
35. M. Ma, P. Zhu, F. Pi, J. Ji and X. Sun, *J. Electroanal. Chem.*, 775 (2016) 178.
36. R. Domínguez-González, L. González Varela and P. Bermejo-Barrera, *Talanta*, 118 (2014) 269.
37. Z. G. Liu and X. J. Huang, *TrAC Trends Anal. Chem.*, 60 (2014) 35.
38. I. Touridomon, A. Karim, D. Mertens, S. N. Ronkart and J. Kauffmann, *Talanta*, 152 (2016) 340.
39. L. Xiao, G. G. Wildgoose and R. G. Compton, *Anal. Chim. Acta,* 620 (2008) 49.
40. B. Maranowski, M. Strawski, W. Osowiecki and M. Szklarczyk, *J. Electroanal. Chem.*, 752 (2015) 59.
41. J. Han, L. Jiang, F. Li, P. Wang, Q. Liu, Y. Dong, Y. Li, Yueyun and Q. Wei, *Biosens. Bioelectron.*, 77 (2016) 1111.
42. T. M. Young, D. Jagner and G. E. Batley, *Anal. Chim. Acta,* 381 (1999) 213.
43. Z. Jia, A. O. Simm, X. Dai and R. G. Compton, *J. Electroanal. Chem.*, 587 (2006) 253.
44. R. Baron, B. Šljukić, C. Salter, A. Crossley and R. G. Compton, *Russ. J. Phys. Chem. A*, 81 (2007) 1447.
45. A. Salimi, H. Mamkhezri, R. Hallaj and S. Soltanian, *Sensors Actuators B Chem.*, 129 (2008) 254.
46. M. Kopanica and L. Novotný, *Anal. Chim. Acta*, 368 (1998) 218.

47. 47. Q. Zhang, X. Li, H. Shi and Z. Yuan, *Electrochim. Acta*, 55 (2010) 4721.
48. S. H. Tan and S. P. Kounaves, Electroanalysis, 10 (1998) 368.
49. D. Van Halem, S. A. Bakker, G. L. Amy and J. C. Van Dijk, *Drink. Water Eng. Sci.*, 2 (2009) 34.