Development of an amperometric sensor based on the synergistic action between alginic acid and nPEDOT on a gold nanoparticle-modified screen–printed carbon electrode for As(III) determination in natural water samples

Claudia Núñez[1,], Rodrigo Segura[1], Verónica Arancibia[2]*

[1] Universidad de Santiago de Chile, Facultad de Química y Biología, Santiago. Chile.
[2] Universidad Bernardo O´Higgins, Centro Integrativo de Biología y Química Aplicada (CIBQA), Santiago 8370993. Chile
[*]E-mail: ctnunez@uc.cl; Rodrigo.segura@usach.cl; darancim@uc.cl

A simple and fast amperometric sensor for As(III) determination has been developed using alginic acid (AA) and nPEDOT on gold nanoparticle–modified screen–printed carbon electrodes (AuNP–SPCE). To obtain a selective method for As(III) determination, the effects of various parameters, such as pH, supporting electrolyte, AA and nPEDOT concentration (C_{AA}, C_{nPEDOT}), and applied potential (E_{app}), were studied. The optimal experimental conditions were chosen to be as follows: phosphoric acid pH 3.0 (0.05 mol L^{-1}); C_{AA}: 0.50 µg L^{-1} and C_{nPEDOT} 50% w/v (E_{app}: -0.30V). The peak current was proportional to the As concentration between 5.0 and 25.0 µg L^{-1} (R=0.9903), with a detection limit (DL, 3σ) of 2.7 µg L^{-1} and a sensitivity of 0.0481 mA/µg L^{-1}. Four different modified electrodes were used in this study: AuNPs-SPCE, AA/AuNPs-SPCE, nPEDOT/AuNPs-SPCE and AA/nPEDOT/AuNPs-SPCE. It was found that in the presence of AA and nPEDOT, the current of the arsenic signal was higher than that obtained using each of the compounds individually. AA allowed the adsorption of the arsenic on the electrode obtaining good sensitivity and nPEDOT, an excellent conductor, improved the electronic transfer in the electroanalytical system. The advantages of this new procedure are fast complexation kinetics, high specificity, simplicity and speed. Finally, the best electrode (AA/nPEDOT/AuNPs-SPCE) was applied to the determination of total arsenic in a water sample from the Loa River (North zone) and two samples from the Central zone (Santiago and Fifth region) with satisfactory results. Values obtained were compared with an ICP-MS method. To determine As_{total}, As(V) was reduced in the presence of thiosulfate in an acidic medium.

1. INTRODUCTION

Arsenic is a ubiquitous metalloid well known for its toxicity and various adverse health effects. The adverse effects depend on the chemical form (organic and inorganic arsenic) and oxidation states (−3, 0, 3, and 5) that occur in the environment. In fact, As(III) is approximately 100 times more toxic than As(V), and methylated compounds that contain trivalent arsenic are more cytotoxic and genotoxic than arsenite. Inorganic arsenic compounds have been classified as Group 1 carcinogens by the International Agency for Research on Cancer, and the WHO has promulgated a more stringent drinking water standard for arsenic with a maximum permissible concentration of 10 µg L^{-1}. This metalloid is usually found in water, soil and air from natural and anthropogenic sources originating from mining activities, fertilizer application, arsenical pesticide usage and fossil fuel combustion. Consumption of water with high concentrations of this metalloid over an extended period of time causes serious diseases, abnormal skin pigmentation, diabetes, hypertension, neural injury, cardiovascular and peripheral vascular disease anomalies, lung fibrosis, hematological disorders and carcinoma. In various countries worldwide, problems with high levels of arsenic have been identified. For twelve years (1959–1970), the inhabitants of the city of Antofagasta (Second Region of Chile) have consumed water and food with concentrations of arsenic greater than 500 µg L^{-1} [1–6].

Electroanalytical techniques have important advantages that include speed, selectivity, sensitivity, low detection limits, short analysis time, minimal sample pretreatment-and low equipment cost compared with atomic spectrometry, and they are adequate for on-site sample monitoring. Several electroanalytical techniques have been developed for determination of arsenic, among these, the most sensitive are anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) whose sensibility are attributed to the combination of an effective preconcentration step, in which arsenic is accumulated onto the electrode from the solution. Similarly, to improve the sensitivity of amperometric techniques, one possibility would be to modify the electrode with specific adsorbents for arsenic [7–10].

Lessonia nigrescens (Phaeophyceae) is a brown alga constitutive of kelp that is abundant along the coast of Chile. This alga has a strong affinity for metal binding due to the presence of alginate in its structure. It may be present in both the cell wall matrix and in the mucilage or intercellular material and can constitute between 10% and 40% of the dry weight (untreated) of the algae. Alginic acid is the common name given to a family of linear polysaccharides containing 1,4-linked β-D-mannuronic (M) and α-L-guluronic (G) acid residues arranged in a nonregular, blockwise order along the chain. Alginates alone and alginates modified with divalent cations (due to cooperative binding between the α-L-guluronic block, creating ionic cross-linking of polysaccharide chains that leads to the formation of hydrogels or with β-FeOOH (akaganeite) forming porous tunnels) have been investigated as good absorbents due to their high affinity toward arsenic derived from their porous tunnel structure [11–14]. Due to these properties, AA could be suitable for modifying the electrode and concentrating the arsenic.

On the other hand, to improve the electronic transfer in the electroanalytical system, it is possible to use poly(3,4-ethylenedioxythiophene) (nPEDOT), which is a very good conductive polymer with electrochemical stability, high conductivity, and a low oxidation potential of the monomer that acts as an electronic mediator as a result of its rich electron cloud. The electrodeposition of Pd nanodendrites

on the surface of PEDOT-coated carbon paper electrodes has been reported for As(III) detection [15–20].

The main objective of the present work was to fabricate a sensor by coating AA, in hydrogel form, mixed with nPEDOT over the surface of a screen-printed electrode modified with Au nanoparticles and optimize the amperometric methodology for determining arsenic in natural water samples. The procedure was then validated using uncontaminated drinking water and applied to the analysis of real samples from Loa river and irrigation water from Santiago and Ventanas (Chile) with satisfactory results (n=3). Values obtained were compared with an ICP-MS method.

2. EXPERIMENTAL PART

2.1. Apparatus

Amperometric measurements were made with a CHI 600E electrochemical system (Austin, TX) with a gold nanoparticle-modified screen-printed carbon electrode DRP–110GNP purchased from Dropsens and modified with alginic acid (AA) and nPEDOT. A silver pseudo reference electrode and carbon as auxiliary electrode completed the circuit. pH was measured with an Orion model 430 pH meter.

2.2. Chemicals and materials

Poly(3,4-ethylenedioxythiophene) (nPEDOT) (CAS:126213-51-2) and alginic acid (AA) (CAS:9005-38-3) were purchased from Sigma–Aldrich. The As(III) standard solution of 1000 mg L^{-1} was provided by Fluka (CAS 39436). 85% w/w Phosphoric acid and 30% w/w sodium hydroxide solution (Suprapur, Merck) were used to prepare the supporting electrolyte. The pH was adjusted with 4.0 mol L^{-1} sodium hydroxide solution. Interference studies were made by diluting standard solutions (1000 mg L^{-1}. CertiPUR, Merck) of Al, Be, Bi, Ca, Cd, Co, Fe, K, Ni, Li, Mg, Mn, Mo, Pb, Sb, Se, Tl and Zn. The method was applied to the determination of total arsenic in natural water from different zones in Chile. The total arsenic concentration was obtained after reduction of As(V) to As (III) mixing river water sample with 0.4 mol L^{-1} $Na_2S_2O_3$ in HCl medium. All solutions were prepared with deionized water (LiChrosolv, Merck CAS: 7732–18–5).

2.3. Preparation of electrochemical sensor

The working electrode surface was modified by depositing 5.0 µL of a mixture of nPEDOT and AA (2.5 µL of nPEDOT suspension $\approx$ 96,8 % w/v and 2.5 µL alginic acid 1.00 µg L^{-1} incubated for 60 minutes at room temperature). Afterward, AA/nPEDOT/AuNPs-SPCE was immersed in phosphoric acid (0.05 mol L^{-1} pH 3.0) for 15 minutes under constant stirring. Finally, the electrode was stored at 4 °C until use.

2.4. Electrochemical measurements

Cyclic voltammetry (CV) was performed from –800 to 800 mV with a sweep speed of 50 mV s–1. Amperometric detection of As(III) was carried out at -300 mV. The electrochemical cell (10.0 mL) contained 0.05 mol L^{-1} phosphoric acid at pH 3.0. The calibration curves, linear ranges, detection limit, and sensitivity of the method were obtained using the optimal parameters employed in the preparation of the electrochemical sensor (AA/nPEDOT/AuNPs-SPCE) and their application in As(III) detection.

2.5. Analysis of As(III) in natural water samples

The developed sensor was applied to the determination of As(III) in samples of diverse natural water bodies from Chile (Ventanas, fifth region), the Loa River (north zone) and the Pedro de Valdivia, Santiago zone). First, arsenic species present were reduced by adding 80 µL of 0.40 mol L^{-1} $Na_2S_2O_3$ to 5.0 mL of sample and brought to a final volume of 10.0 mL in an acidic medium. An aliquot of these samples was added to the cell, and As(III) was determined using the standard addition method to eliminate matrix effects.

2.6. Limits of detection and quantitation (DL, QL)

The DL was calculated using the approximation of Miller and Miller [21] for calibration curves with $X_{DL} = 3 \sigma_{XY}/b$, where σ_{XY} is the standard deviation of the calibration curve and b is the slope.

3. RESULTS AND DISCUSSION

In the work reported here, we studied a simple alternative sensor applicable for routine monitoring of arsenic in natural water; for this, we used a commercial AuNP-SPCE. The positive effect of gold nanoparticles in the electrochemical detection of As(III) has been widely described [22–26]. We investigated the influence of the addition of nPEDOT and alginic acid to this working electrode and developed an analytic method for the determination of total arsenic in natural water samples after the reduction of As(V) to As(III).

3.1. Electrochemical behavior of AA/nPEDOT/AuNPs-SPCE sensor

Initially, the electrochemical properties of alginic acid (AA) and nPEDOT were studied by modifying a commercial AuNP-SPCE as described in Section 2.3. To evaluate the interface properties of the modified electrode, the stepwise fabrication of the sensor (AuNPS-SPCE and nPEDOT/AuNPs-SPCE) was monitored by cyclic voltammetry (CV). For the electrochemical measurement, 10.0 mL of KCl solution (0.1 mol L^{-1}) containing 5 mmol L^{-1} $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ was pipetted into a voltammetric cell, and CVs were obtained with all of the electrodes. Fig. 1A shows CVs of AuNPs-SPCE,

nPEDOT/AuNPs-SPCE and AA/nPEDOT/AuNPs-SPCE. The electrode modified with nPEDOT showed an increase in the magnitude of current of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ compared to the AuNP-SPCE, indicating an acceleration of the electron transfer on the electrode surface. However, after AA addition, the redox current decreased significantly, indicating that AA limited electron transfer. On the other hand, the potential values E_{pa}/E_{pc} were 0.253/0.024, 0.266/0.019, and 0.119/0.062 V/V for AuNPs–SPCE, nPEDOT/AuNPs–SPCE, and AA/nPEDOT/AuNPs-SPCE, respectively. As seen in these CVs, when AA was added to a gold nanoparticle screen–printed carbon electrode modified with nPEDOT, the reversibility of the model system $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ increased markedly, and the signal was shifted to less positive potentials.
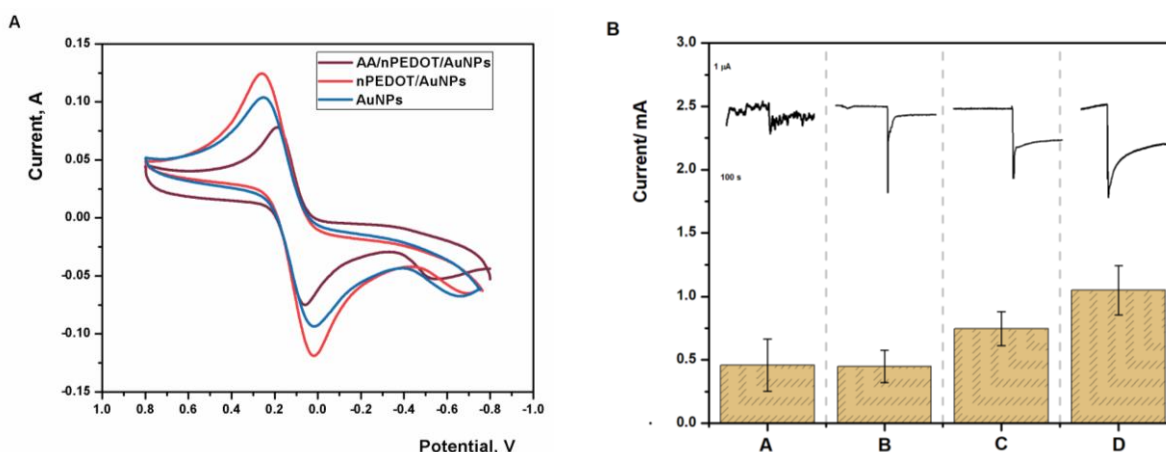

Figure 1. A) Cyclic voltammogram study of surface modification of electrode in $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ 5.00 mmol L^{-1} in KCl 0.10 mol L^{-1} Amperometry Conditions: Phosphate solution 0.50 mol L^{-1} pH 5.0; E_{app} -0.30 V. B) Study of the amperometric response of 100 µgL^{-1} As(III) over different electrochemical platforms: (A) AuNPs-SPCE, (B) nPEDOT/AuNPs-SPCE, (C) AA/AuNPs-SPCE, and (D) AA/nPEDOT/AuNPs-SPCE.

The electrochemical behavior was studied through the arsenic amperometric response. Fig. 1B shows the relationship between the response current of the sensor and 100 µg L^{-1} As(III) using AuNPs-SPCE, nPEDOT/AuNPs-SPCE, AA/AuNPs-SPCE and AA/nPEDOT/AuNPs-SPCE. The combination of nPEDOT with AuNPs improves the properties of the sensor surface due to the effect that arises from the combination of both nanomaterials decreasing the resistance of the system. The ability of AA and its derivatives to efficiently chelate metal ions has been reported [27]; hence, the addition of AA on the surface electrode could increase the signal current of As(III) due to the complex formed with the polysaccharide on the surface electrode.

It was found that due the synergistic effect between AA and nPEDOT, the peak current of the arsenic signal was higher than that obtained using each of the compounds individually. AA allowed the accumulation of the arsenic on the electrode by complex formation obtaining good sensitivity and nPEDOT, a conducting polymer, improved the electronic transfer in the electroanalytical system.

3.2. Electrochemical behavior of AA/nPEDOT/AuNPs-SPCE sensor
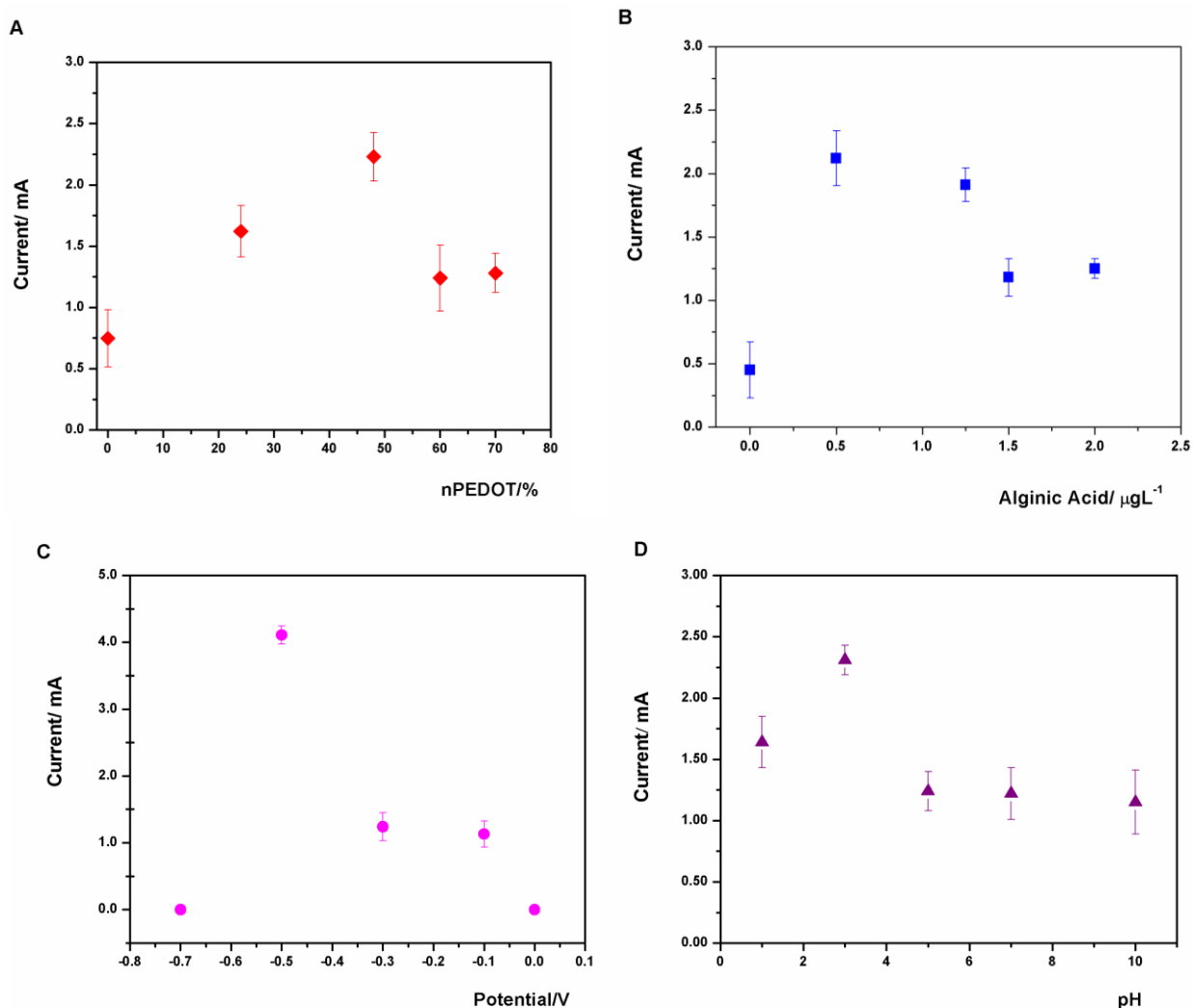
Figure 2. Effect of the A) nPEDOT concentration B) alginic acid concentration C) potential and D) pH of phosphate solution on the amperometric response of 100 μgL^{-1} As(III). Initial amperometry conditions: phosphate solution 0.50 mol L^{-1} pH 5.0; E_{app} -0.30 V.

The optimal conditions of biosensor fabrication and amperometric measurements were investigated through the reduction current response of 100 μg L^{-1} As(III) using an initial phosphate solution of 0.05 mol L^{-1} at pH 5.0 and applying a potential of -0.30 V. The variables studied were AA/nPEDOT concentration, applied potential and pH.

The concentration of nPEDOT was evaluated over the 0 to 70% w/v range, and a fixed concentration of AA (0.50 µg L-1) was added. Fig. 2A shows the current peak increments until 50% w/v; higher concentrations generate a negative effect, decreasing the signal current due to increased system resistance.

On the other hand, the optimal concentration of AA was evaluated in the 0 to 2.0 µg L^{-1} range, fixing the nPEDOT concentration to 50% w/v, as shown in Fig. 2B. The amperometric response showed a maximum at 0.50 µg L^{-1}, and higher concentrations hindered electronic transfer due to overlap.

The effect of the applied potential on the amperometric response was examined over a -0.70 to 0 V range. Figure 2C shows a maximum signal at -0.50 V; however, it is unstable and hinders recovery of electrode activity. The potential was fixed at -0.30 V. The influence of pH was tested in the 1.0 to 10.0 range using 0.05 mol L^{-1} phosphoric acid, adjusting the pH with 4.0 mol L^{-1} sodium hydroxide solution (Fig. 2D). However, it was found that at an acidic pH, the reduction current was significantly higher than that at a pH above 5.0, probably due to the promotion of the formation of As-AA complexes on the electrode surface. The optimal pH was fixed to 3.0.

3.3. Analytical performance of the AA/nPEDOT/AuNPs-SPCE sensor.
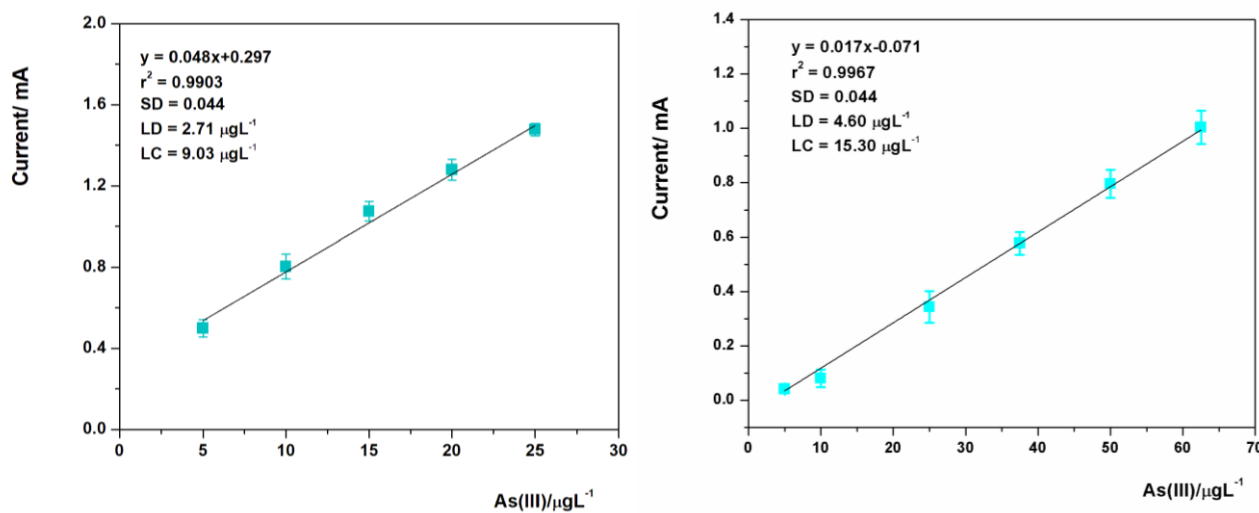
Figure 3. A) Calibration curve plot current peak *vs.* by successive additions of As(III) from 5.0 to 25.0 μgL^{-1}. Conditions: Phosphoric acid 0.50 mol L^{-1} at pH 3.0, applied potential of -0.30 V, AA 0.50 μgL^{-1}, nPEDOT 50 % w/v. B) Calibration curve plot current peak *vs.* successive additions of As(III) from 5.0 to 65.0 μgL^{-1}. Conditions: Phosphoric acid 0.50 mol L^{-1} at pH 3.0, applied potential of -0.30 V, AA 0.50 μgL^{-1}, nPEDOT 50 % w/v.

Optimal fabrication of AA/nPEDOT/AuNPs-SPCE sensor and analytical conditions were used to determined lineal range, calibration curves of As(III) and method sensitivity. Under these conditions 0.50 μg L^{-1} AA; 50 % w/v nPEDOT; 0.05 mol L^{-1} phosphoric acid pH 3.0 and applying a potential of -0.30 V the signal current peak was proportional to the concentration of As over the 5.0-25.0 μg L^{-1} range. The corresponding calibration graph followed the linear equation y=0.297 + 0.048x (R: 0.9951, n=5) with a 3σ detection limit of 2.7 μg L^{-1} and 10σ quantification limit of 9.0 μg L^{-1}. The sensitivity was 0.048± 0.002 mA/μg L^{-1} and intercept was 0.297 ± 0.05 mA/μg L^{-1} (Fig.3a). The linear calibration plot can be extended up to a concentration of 65.0 μg L^{-1} (y=-0.071 + 0.017x (R: 0.9983, n=6) but the 3σ detection limit was 4.6 μg L^{-1} and the intercept is negative (Fig.3b). At higher concentrations the linearity remains, but the slope of the calibration curve is lower. The DL obtained in the present study was slightly older to those reported previously, using screen printed electrodes as in Table 1.

Table 1. Comparative study on the performance of different screen printed electrodes used for arsenic detection.

Electrode	As(III), As(V)	Detection method	Sample	Detection limit ($\mu g\ L^{-1}$)	Accumulation time (s)	Ref.
AF/AuNP/SPCE	As(III)	AD	water	137.8	-	28
LA/Cyst/AuNP/SPCE	As(III)	SWASV	water	3	300	29
AuNP/SPCE	As(III)	SWSV	apple juice	16.73	300	30
ChOx/DWCNTs-Gr/SPE	As(V)	SWV	-	0.29	-	31
Gr/SPE	As(III)	DPV	urine	0.28	-	32
Ag-NP-SPCNFEs	As(V)	DPASV	water	0.6	120	33
SiNPs/SPCE	As(III)	LSASV	water	6.2	300	34
PANI/BiVO$_4$/SPCE	As(III)	DPASV	blood	0.0072	60	35
Ag/SPCE	As(III)	SWASV	water	8.4	180	36
Fe$_3$O$_4$/rGO/SPCE	As(III)	SWASV	soil	0.3	120	37
CB-AuNPs/SPE	As(III)	ASV	water	0.4	120	38
LLAu/SPE	As(III) As(V)	SIASV	water	0.03	120	26
Ibu-AuPNFs/SPE	As(III)	CV	water	0.018	-	24
AuNPs/SPE	As(III)	ASV	water	0.4	120	39
Ach/SPCE	As(III)	AD	water	0.82	-	40
PtNPs/SPCE	As(III)	CV	water	5.68	-	41
SPAuE	As(III)	SWASV	water	2.5	60	42
PBSPE	As(III)	FIA	water	1.87	-	43
PLA/AuNP/SPE	As(III)	DPASV	water	0.09	130	44
AA/nPEDOT/AuNPs/SPCE	As(III)	AD	water	2.7	-	This work

AF/AuNPs–SPCE: *Alcaligenis faecalis* bacteria on gold nanoparticle–modified screen–printed carbon electrode. LA,Cyst/AuNP/SPCE: Lipoic acid and L-cysteine on gold nanoparticle–modified screen–printed carbon electrode. ChOx/DWCNTs-Gr/SPE: Cholesterol oxidase enzyme on double-walled carbon nanotubes-graphene modified screen–printed electrode. Gr/SPE: screen–printed graphene electrode. Ag-NP-SPCNFEs: Carbon-nanofiber-based screen-printed electrodes modified with silver nanoparticles. SiNPs/SPCE: Silica nanoparticles-modified screen-printed carbon electrode. PANI@BiVO$_4$/SPCE: Polyaniline coated bismuth vanadate modified screen-printed carbon electrode. CB-AuNPs/SPE: Carbon black-gold nanoparticles modified screen-printed electrode. LLAu/SPCE: Long-lasting gold-modified screen-printed carbon electrode. Ibu-AuPNFs/SPE: Ibuprofen derived gold nanoflowers/nanotructures modified screen-printed electrode. Ach/SPCE: Acetylcholinesterase-modified screen-printed carbon electrode. PBSPE: Prussian blue-modified screen-printed electrode. PLA/AuNP/SPE: Poly(l-lactide) stabilized gold nanoparticles modified screen-printed electrode.

Durai and Badhulika [35] used a SPCE modified with bismuth vanadate nanoflakes coated with polyaniline for the determination of As(III) obtaining one of the best detection limits presented in Table 1 (0.0072 $\mu g\ L^{-1}$. t$_{acc}$: 60s). Sirajuddin et al. [24] used a SPE modified with Nafion-ibuprofen-gold nanostructures which was very effective in the determination of As(III) in water samples obtaining detection limits of 0.018 $\mu g\ L^{-1}$. Chailapakul et al [26] developed a method for speciation of As(III) and As(V) applying sequential injection/anodic stripping voltammetry with a long-lasting gold-modified SPCE obtaining a DL of 0.03 $\mu g\ L^{-1}$ (t$_{acc}$: 120 s). Zen et al. [44] used Poly(l-lactide) stabilized gold nanoparticles to modify a disposable SPCE for the detection of As(III) by DPASV obtaining a DL of 0.09 $\mu g\ L^{-1}$ (tacc: 130 s). On the other hand, Kurup et al. [30] used a simple gold nanoparticle modified

screen printed carbon electrode (AuNPs/SPCE) obtaining a DL of 16.73 μg L^{-1}. In our work by adding AA and PEDOT we reduce DL to 2.7 μg L^{-1}.

3.4. Selectivity and stability of the AA/nPEDOT/AuNPs-SPCE electrochemical sensor.

In order to determinate the of AA/nPEDOT/AuNPs-SPCE the interference of Cu(II), Pb(II) and Cd(II) due that this ions form complexes with AA (Fig. 4A) was evaluated. The sensor did not show significant increase in current response probably due to these ion present electrochemical reactions at potentials more negative, therefore they did not interfere with the determination of As. Furthermore, the effect of the presence of Mg, Mn, Fe, Bi, Zn, and Se were studied a higher concentration (100 μg L^{-1}) compared with As(III) (20 μg L^{-1}). The sensor did not show a significant signal and the amperometric response of was retained in a 98% was retained (Fig. 4B).

The stability and reproducibility were evaluated using 50 ug L^{-1} As(III) solution. For determine the reproducibility were prepared independently 5 electrodes, the relative standard deviation (RSD) was 5.5% (Fig. 4C). The stability was evaluated by measuring the As(III) amperometric response and the signal current peak remains during only 3 days and showed an abrupt decrease and not being able to regenerate the activity.
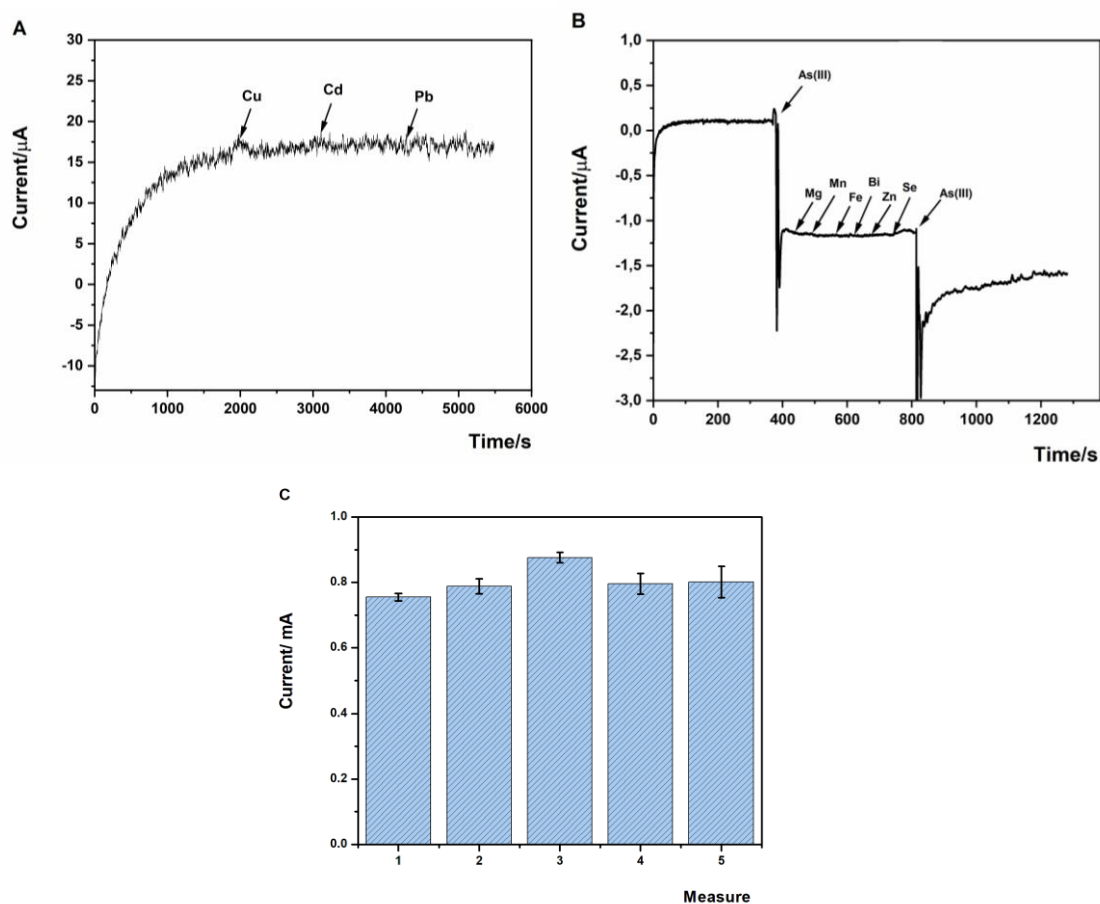
Figure 4. A) Study of interference of different metals on AA/nPEDOT/uNPs-SPCE sensor. B) Study of interference of different metals with As(III) solution of 20 μg L^{-1}. C) Study of reproducibility using 50 μg L^{-1} As(III). Conditions: Phosphoric acid 0.50 mol L^{-1} at pH 3.0, applied potential of -0.30 V, AA 0.50 μg L^{-1}, nPEDOT 50 % /w/v.

3.5 Application of the AA/nPEDOT/AuNPs-SPCE sensor in analysis of total arsenic on natural water samples

The novel electrode AA/nPEDOT/AuNPs-SPCE was validated using an aliquot of tap water (spiked with 50.0 μg L^{-1} of As(III)) and the determination was carried out using the standard addition method obtaining an As concentration of 51.6 ± 0.2 μg L^{-1}. Then, a new modified electrode was used in the determination of As$_{total}$ in samples of natural waters from North, South and Central Chile. To determine As$_{total}$, As(V) was reduced in the presence of thiosulfate in an acid medium. The results obtained are shown in Table 2 and Fig.5. These values were compared with measurements carried out by ICP-MS indicated that the sensor performance can be considered as a promising alternative for monitoring of total arsenic in natural water sample.

Table 2. Analysis of total As in diverse water body samples from Chile with the AA/nPEDOT/AuNPs-SPCE sensor under optimized conditions and values reported by ICP-MS.

Sample	As(T), μg L^{-1}	
	This work$^{(*)}$	ICP-MS
Loa River (North zone)	929 ± 1.76	800
Ventanas (Fifth region zone)	35 ± 0.08	43
Santiago Zone	17 ± 0.06	15

$^{(*)}$ n = 3; α = 0.05
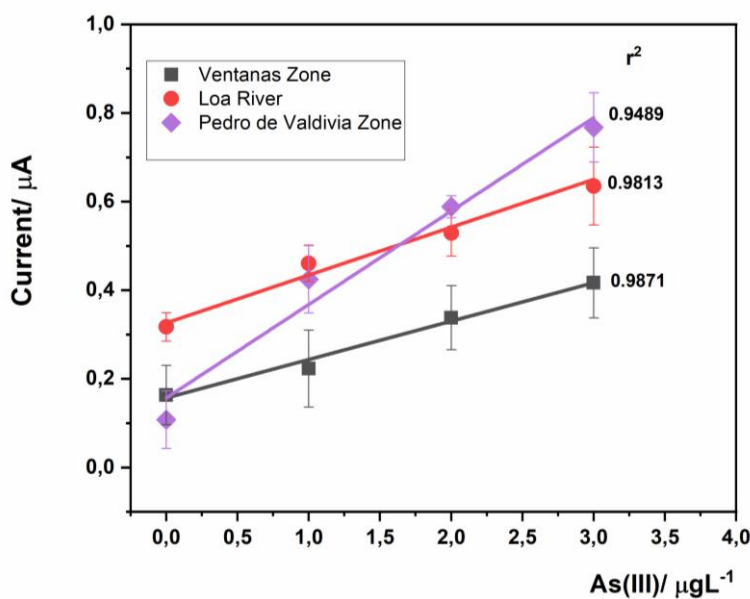
Figure 5. Calibration curve plot current peak of real samples by successive additions of As(III) from 10.0; 20.0 and 30.0 μgL^{-1}. Conditions: Phosphoric acid 0.50 mol L^{-1} at pH 3.0, applied potential of -0.30 V, AA 0.50 μgL^{-1}, nPEDOT 50 % w/v.

4. CONCLUSIONS

In the present work a simple methodology for arsenic determination modifying an AuNPs-SPCE with nPEDOT and AA is report. The dopping of AA/nPEDOT with AuNPs-SPCE offered a specific sensor due to formed an As-AA complex on electrode surface. The presence of AA allowed the adsorption of the complex on the electrode and the synergy between nPEDOT and AuNPs allow the electronic transfer supply a good sensitivity. The advantages of this new procedure are fast complexation kinetics, high specificity, simplicity and speed. The method can be applied to both natural water samples adding a small volume of sample and avoid the interference due to the matrix.

References

1. WHO (World Health Organization). (2010). http://www.who.int/ipcs/features/arsenic.pdf?ua=1
2. P.L. Smedley, D.G. Kinniburgh, *Appl. Geochem*., 17 (2002) 517.
3. B.K. Mandal, K.T. Suzuki, *Talanta*, 58 (2002) 201.
4. J. Yañez, V. Fierro, H.Mansilla, L. Figueroa, L. Cornejo, R. Barnes, *J. Environ. Monit*., 7 (2005) 1335.
5. Guidelines for Drinking−water Quality. Fact Sheet N°372, December, http://www.who.int/mediacentre/factsheets/fs372/es.
6. T.A. Davis, B. Volesky, A. Mucci, *Water Res*., 37 (2003) 4311.
7. J. Tyson, *ISRN Anal. Chem*., (2013) 835371.
8. K.A. Francesconi, D. Kuehnelt, *Analyst*, 129 (2004) 373.
9. A.N. Anthemidis, N.P. Kalogiouri, *Anal. Lett*., 46 (2013) 1672.
10. B.J. Sanghavi, N.S. Gadhari, P.K. Kalambate, S.P. Karna, A.K. Srivastava, *Microchim. Acta*, 182 (2015) 1473.
11. M.S. Shoichet, R.H. Li, M.L. White, S.R. Winn, *Biotechnol. Bioeng*, 50 (1996) 374.
12. E. Deliyanni, D. Bakoyannakis, A. Zouboulis, K. Matis, *Chemosphere*, 50 (2003) 155.
13. E. Deliyanni, D. Bakoyannakis, A. Zouboulis, E. Peleka, *Sep. Sci. Technol*., 38 (2003) 3967.
14. E. Muñoz, S. Palmero, *Talanta,* 65 (2005) 613.
15. A.K. Sakira, T. Issa, E. Ziemons, B. Dejaegher, D. Mertens, P. Hubert, J.M. Kauffmann, *Electroanalysis*, 27 (2015) 309.
16. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, *Adv. Mater*., 12 (2000) 481.
17. P. Yáñez-Sedeño, J.M. Pingarrón, *Anal. Bioanal. Chem*., 382 (2005) 884.
18. T. Rajesh, D. Ahuja, S. Kumar. *Sens. Actuators B Chem*., 136 (2009) 275.
19. S.S Kumar, J. Mathiyarasu, K.L.N. Phani, V. Yegnaraman, *J Solid State Electrochem*., 10 (2006) 905.
20. E. Iwuoha, D. Saenz de Villaverde, N. Peña-García, M.R. Malcolm, J.M. Pingarrón, *Bioelectron.* 12 (1997) 749.
21. J.C. Miller, J.N. Miller in *Statistics for Analytical Chemistry, 2ed., Ellis Horwood*, London, 1988.
22. A.A. Abdelwahab, *Electroanalysis*, 28 (2016) 1901.
23. M. Khairy, D.K. Kampouris, R.O. Kadara, C.E. Banks, *Electroanalysis*, 22 (2010) 2496.

24. S.S. Hassan, S. Sirajuddin, A.R. Solangi, T.G. Kazi, M.S. Kalhoro, Y. Junejo, Z.A. Tagar, N.H. Kalwar, *J. Electroanal. Chem*., 682 (2012) 77.
25. K. Pungjunun, S. Chaiyo, I. Jantrahong, S. Nantaphol, W. Siangproh, O. Chailapakul, *Microchim Acta*, 185 (2018) 324.
26. E. Punrat, S. Chuanuwatanakul, T. Kaneta, S. Motomizu, O. Chailapakul, *Talanta,* 116 (2013) 1018.
27. F. Shanura, K.K. Asanka, K. Seo-Young, L. Jung-Suck, J. You-Jin, *Int. J. Biol. Macromol*., 106 (2018) 330.
28. C. Núñez, J.J. Triviño, V. Arancibia, *Talanta,* 223 (2021) 121702.
29. A.N. Jijana, N. Mphuthi, P. Shumbula, S. Vilakazi, L. Sikhwivhilu, *Electrocatalysis* 12 (2021) 310.
30. C. Sullivan, D. Lu, A. Senecal, P. Kurup, *Food Chem.,* 352 (2021) 129327
31. P.N. Duc-Duoc, N. Hai-Binh, T. Van Hau, C. Thi-Thanh, P. Van-Trinh, N. Viet-Tuyen, N. Van-Quynh, N. Van-Tu, V. Duc-Chinh, V. Thi-Thu, P. Duc-Thang, P. Ngoc-Minh, N. Van-Chuc, *J. Hazard. Mater.*, 400 (2020) 123185.
32. C. Núñez, J.J. Triviño, R. Segura, V. Arancibia, *Microchem. J*., 159 (2020) 105393.
33. K. Torres-Rivero, C. Pérez-Ràfols, J. Bastos-Arrieta, A. Florido, V. Martí, N. Serrano, *Nanomaterials* 10 (2020) 1280.
34. S. Ismail, N. Azah-Yusof, J. Abdullah, S.F. Abd-Rahman, *Materials*, 13 (2020) 3168.
35. L. Durai, S. Badhulika, *Mat. Sci., & Eng. C,* 111 (2020) 110806.
36. S.P. Méndez-Cortés, C.A. Galán-Vidal, J.A. Rodríguez-Ávila, G.A. Álvarez-Romero, M.E. Páez-Hernández, *J. Mex. Chem. Soc*. 62 (2018) 214.
37. Z. Xie, J. Xu, F. Xie, S. Xiong, *Anal. Sci*., 32 (2016) 1053.
38. S. Cinti, S. Politi, D. Moscone, G. Palleschi, F. Arduini, Electroanalysis 26 (2014) 931.
39. M. Khairy, D.K. Kampouris, R.O. Kadara, C.E. Banks, *Electroanalysis,* 22 (2010) 2496.
40. S. Sanllorente-Méndez, O. Domínguez-Renedo, M.J. Arcos-Martínez, *Sensors*, 10 (2010) 2119.
41. S. Sanllorente-Méndez, O. Domínguez-Renedo, M.J. Arcos-Martínez, *Electroanalysis*, 21 (2009) 635.
42. S. Laschi, G. Bagni, I. Palchetti, M. Mascini, *Anal. Lett*., 40 (2007) 3002.
43. J.-M. Zen, P.-Y. Chen, A.S. Kumar, *Anal. Chem.*, 75 (2003) 6017.
44. Y.-S. Song, G. Muthuraman, Y.-Z. Chen, C.-C. Lin, J.-M. Zen, *Electroanalysis*, 18 (2006) 1763.