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(Article begins on next page)

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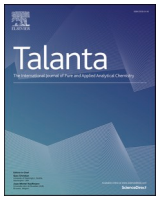

# Development of a portable method for monitoring and speciation of arsenic in aquatic systems by anodic stripping voltammetry: Applications to real samples

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ABSTRACT

The aim of this study was to develop a differential pulse anodic stripping voltammetry (DPASV) method for the rapid, sensitive and cost-effective determination and speciation of inorganic arsenic in aquatic environments. The electrochemical determination of arsenite and arsenate was investigated using a rotating solid gold electrode (SGE). As(III) was selectively determined at +0.1 V by ASV after a deposition at −0.3 V. The total As content (As (V) + As(III)) was electrochemically reduced at −1.2 V by nascent hydrogen to $As^0$, and then As(V) was evaluated indirectly by subtraction. Electrochemical reduction of As(V), instead of chemical reduction, was chosen to minimize the consumption of chemical reagents, reduce analysis time and provide a method suitable for on-site analysis. First, the operating parameters were optimized, and the method was characterized in terms of selectivity, sensitivity, linearity, precision and accuracy. A Limit of Detection (LOD) of 0.10 μg $L^{-1}$ was found for the developed technique for $As_{(tot)}$. The method was then applied to the direct quantitative determination and speciation of inorganic arsenic in real water samples; the results obtained showed satisfactory agreement with those produced by the hydride generation technique coupled with inductively coupled plasma atomic emission spectroscopy (HG-ICP-OES). Subsequently, the voltammetric determination of arsenic was explored with a portable potentiostat to evaluate the reliability of the procedure for on-site detection.

## 1. Introduction

Arsenic (As) is a natural occurring semimetal, which is widely distributed on the earth's crust with an average concentration of 1.8 mg $kg^{-1}$ [1]. In nature arsenic exists in its native form and in the form of inorganic and organic compounds. In natural aquatic systems, the presence of As is mainly due to geogenic and geochemical events: As minerals associated with metamorphic, sedimentary and igneous rocks undergo chemical erosion reactions when in contact with water and/or air; these processes transform the species contained in the minerals into its inorganic forms, arsenites and arsenates, which are released into aquatic ecosystems, surface waters or groundwaters [2]. Not only biogeochemical processes but also anthropogenic activities may lead to the contamination of natural waters. Since As is often found in association with other elements in mineral oxides, some of its inorganic compounds can be mobilised in natural waters by anthropogenic activities: the main contribution is due to mining activities and refining processes of mined metals [3]. In natural waters arsenic compounds mainly exist as oxyanions, thioanions or as intermetallic complexes. Furthermore, inorganic As(V) is more abundant than As(III) under aerobic conditions typical of surface waters, whereas non-negligible concentrations of metastable As(III) species can be found under moderately reducing conditions and/or intense biological activity [4]. Thus, the chemical and reactivity of arsenic compounds depend on environmental conditions (temperature, pH, redox conditions and biotic activity) [1]. Organic arsenic species are generally at least ten times less abundant than inorganic ones in natural aquatic systems; their formation is entirely due to the metabolic activity of the biota, which is able to convert inorganic compounds into methylated As species (monomethylarsonic acid and dimethylarsinic acid), arsenobetaine and

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**Table 1**
Different electroanalytical method for As determination.

| Electrode | Method | Linear range (μg $L^{-1}$) | Limit of detection (μg $L^{-1}$) | Ref. |
|---|---|---|---|---|
| SGE | DPASV | 0.5–10 | 0.10 | This work |
| Pt macroelectrode | ASV | 4.0–80 | 4.0 | [19] |
| Nano-Au/GCE | LSV | 1.8–75 | 1.8 | [20] |
| AuFe/GCE | SWASV | 10–250 | 1.0 | [21] |
| Mn coated/Au microwire | SWASV | 0–100 nM | 0.2 nM | [22] |
| Au carbon black composite | ASV | 1.5–45 | 0.5 | [23] |
| Au-coated BDD | DPASV | 0.1–40 | 0.005 | [24] |
| AuNPs - SPE | LSV | 0–250 | 0.4 | [25] |
| AuNPs-CNTs | SWV | 0.75–7.5 | 0.1 | [26] |
| MEA-Au electrode | DPASV | 0.2–12; 12 - 300 | 0.02 | [27] |

LSV, Linear sweep voltammetry; SWASV, Square wave anodic strippng voltammetry; SGE, Solid gold electrode; GCE, Glassy carbon electrode; BDD, Boron doped diamond; AuNPs, Au nanoparticles; SPE, Screen-printed electrode; CNTs, Carbon nanotubes, MEA, Mercaptoethylamine.

arsenocholine, arsenosugars and arsenolipids [5,6]. The chemical form in which As occurs in the environment determines its bioavailability and toxicity: inorganic forms are known to be more toxic than organic species, and As(III) compounds are more dangerous than As(V) compounds due to their ability to act as enzyme inhibitors [7]. Prolonged exposure to arsenic results in a number of adverse effects in humans: in addition to its carcinogenic effects, it causes the onset of diseases of the cardiovascular, nervous and endocrine systems [8]. According to the recommendation of the World Health Organization (WHO), the maximum level of inorganic arsenic in drinking water should not exceed 10 μg $L^{-1}$ [9]. Due to the highly toxic nature of its compounds, arsenic occupies a special place in environmental research; in particular the determination of arsenic compounds in aquatic systems at trace and ultra-trace levels (μg $L^{-1}$ and sub μg $L^{-1}$) has become an attractive challenge for analytical chemistry. Total arsenic concentration can be detected by different methods usually coupled with hydride generation (HG) technique as a preconcentration step as well as a means to minimize or eliminate matrix interferences. Generally, the HG technique is coupled with atomic absorption spectroscopy (HG-AAS) [10], atomic emission spectroscopy usually combined with inductively coupled plasma (HG-ICP-AES) [11], atomic fluorescence spectroscopy (HG-AFS) [12], and inductively coupled plasma mass spectrometry (HG-ICP-MS) [13]. Due to the highly selective determination of various arsenic species, chromatography techniques (liquid chromatography (LC) and gas chromatography (GC)) take a special place in environmental research [14]. These traditional laboratory-based techniques require expensive instruments, high operating costs and complicated sample preparation processes involving digestion or clean-up steps, which are time consuming and limit the application for field monitoring [15]. On the other hand, electroanalytical techniques could simultaneously ensure rapid, sensitive and low equipment cost compared with spectrometry, and are the most suitable approach for field analysis [16]. In addition, they can perform speciation analysis of inorganic As(III) and As(V) without previous separation. Voltammetric methods can be easily applied for water samples, instead the application to soil and sediment samples can cause many analytical difficulties due to the need to bring the analyte into solution.

The most common electrochemical methods for arsenic determination are based on anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV) [17]. The use of the former allows one to determine arsenic at μg $L^{-1}$ and sub μg $L^{-1}$ levels, but it has also some disadvantages, such as poor reproducibility due to the usage of a solid electrode, hydrogen evolution during the deposition step, and interference from some electrochemically active ions [10]. In ASV analysis, the gold electrode is the most suitable working electrode (WE) for the determination of As. However, various carbon-based electrodes have been explored as convenient substrates on which gold film or gold nanoparticles (AuNPs) are electro-deposited [18]. Table 1 shows different electroanalytical methods of As determination using different types of electrode and their linear response range.

**Table 2**
List of water samples with their code number, type of water and geographical area of provenance.

| Sample code | Type | Provenance |
|---|---|---|
| IT-1 | Source water for aquaculture | Italy |
| IT-2 | Source water for aquaculture | Italy |
| IT-3 | Tap Water | Italy |
| IT-4 | River water | Italy |
| DEN | Aquaculture water | Denmark |
| TH-1 | Aquaculture water | Thailand |
| TH-2 | Aquaculture water | Thailand |
| TH-3 | River water | Thailand |
| TH-4 | Aquaculture water | Thailand |

The main advantages of the method presented in this study are its simplicity and the applicability for field analysis. In particular a solid gold rotating disk electrode (SGE) for As(III) and total inorganic As determination was investigated. Its main advantages are the high hydrogen overpotential and favorable reversibility, which result in a high, well-defined stripping peak of As [28]. Furthermore, SGEs require no special pre-treatment to activate the active surface, which is advantageous for field analysis. A further advantage of the method, confirming its simplicity, is the fact that electrochemical reduction of As(V), which is generally considered not electroactive except in extreme reductant conditions [5], was performed, so that no reagents or lengthy chemical reactions are required. We optimized the conditions for As(III) and total inorganic arsenic determination by ASV. The procedure was characterized from the point of view of selectivity, sensitivity, limit of detection, linearity, precision and accuracy. Subsequently, some water samples, originating from various geographical areas around the world, were analysed to determine As(III) and As(III) + As(V) concentration. The results obtained showed satisfactory agreement with those produced by an analytical comparison method (HG-ICP-OES). Finally, the voltammetric determination of arsenic with a portable potentiostat was explored, using the same method previously developed, to develop a procedure for on-site detection.

## 2. Experimental

### 2.1. Reagents and materials

High purity water (HPW, 18.2 MΩ cm) was obtained from a Milli-Q, Millipore, device. Analytical grade reagents were used. A 1000 mg $L^{-1}$ stock solution of As(V) (>99,9 %; Sigma-Aldrich, St-Louis, Missouri, USA) was used to prepare 10 mg $L^{-1}$ and 1 mg $L^{-1}$ standard solutions weekly. As(III) standard solution 1000 mg $L^{-1}$ was prepared by dissolving $As_2O_3$ (puriss. Fluka-Garantie Honeywell) in 1 M sodium hydroxide (NaOH), then the pH of the solution was adjusted to about 2 with 5 M HCl. Intermediate solutions were prepared daily. For interference studies metal solutions (Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb) were diluted from 1000 mg $L^{-1}$ stock solutions and a dimethylarsinic acid standard solution 1000 mg $L^{-1}$ was prepared by dissolving $(CH_3)_2As(O)OH$ salt in HPW. Analytical grade hydrochloric acid (HCl) and sulfuric acid ($H_2SO_4$) (Sigma-Aldrich, St-Louis, Missouri, USA) were also used.

The samples analysed during this study include a standard reference material, namely *Trace Elements in Water* NIST 1643f (National Institute of Standard and Technology, U.S. Department of Commerce, Gaithersburg, USA) and natural waters of different types: samples belonging to aquaculture farms from different geographical areas (Italy, Denmark and Thailand), river (Italy, Thailand) and tap water (Italy). All the samples are listed in Table 2.

After collection, samples were frozen in plastic containers; the latter are generally preferred to glass to avoid adsorption phenomena onto the walls. Storage of samples at low temperatures is indicated to reduce both biotic and abiotic processes that may alter the speciation of As species in samples [28]. Prior to analyses, each sample was filtered through a 0.22 μm PTFE syringe filter to separate particulate matter from the solution to be analysed. HPW and tap water were also analysed to assess the accuracy of the method.

### 2.2. Instrumentations and electrodes

Voltammetric analyses were performed with a PGSTAT 10 Eco Chemie (Utrecht, Netherlands) potentiostat coupled to a 663 VA Metrohm (Herisau, Switzerland) stand through the IME 663 interface. The analyser was interfaced with a personal computer; the operational conditions were selected and voltammograms were recorded and processed through the GPES software (General Purpose Electrochemical System). Other analyses were performed using a PalmSens4 portable potentiostat (Palmsens, Houten, Netherlands), interfaced with a laptop computer; the PSTrace 4.6 software was used to select the process parameters. The potentiostat was connected to a KIA-Topolino magnetic stirrer and fed with a portable battery.

The voltammetric cell was the same for the two instruments: it was equipped with a commercial Metrohm SGE (a frontal SGE for As(III) and lateral SGE for As (V)), a platinum counter electrode (CE) and an Ag/AgCl/KCl (3 M) reference electrode (RE). Both units have a deoxygenation system by means of gaseous $N_2$ insufflation.

Hydride generation inductively coupled plasma optical emission spectrometry (HG-ICP-OES) analyses were performed with an ICP-OES OPTIMA 7000 DV (PerkinElmer, Shelton, Connecticut, U.S.A.) spectrometer coupled to a hydride generation system. A solution of 0.5 % w/v sodium borohydride ($NaBH_4$) was used as a reducing agent.

### 2.3. Procedures

#### 2.3.1. Electrode pretreatment

The electrochemical activation of the electrode surface was achieved by cyclic voltammetry (CV) after dipping the electrodes in solutions of $H_2SO_4$ 0.5 M. The gold electrode was polarized between 0.0 and +1.50 V using a scan rate of 200 mV $s^{-1}$; 10 scans were applied. This conditioning procedure improves the quality and repeatability of the As signal, but can also be used to check the condition of the active electrode surface (Figs. S1 and S2). At the beginning of the day, before the electrochemical conditioning, the electrode was kept in a 0.1 M NaOH solution for about 30 min and then washed three times with ethanol and water. The use of NaOH in the pre-treatment procedure is widely adopted in literature [29–31] and is based on the good solubility of arsenic compounds in ionic form in a basic environment; it is assumed that sodium hydroxide can help to remove the As remaining adsorbed on the electrode during the previous analytical procedure. The activation of the electrode was repeated halfway through the day. Following the analysis of each sample, the cell containing the electrodes is filled with a washing solution consisting of $0.5x10^{-3}$ M disodium EDTA, $1.5x10^{-3}$ M NaCl, 0.1 M $HClO_4$, and a potential of +0.60 V is applied for 30 s. The application of an oxidative potential is a cleaning procedure widely reported in literature [32] and aims to achieve the oxidation of any analyte residue present on the electrode.

When a significant loss of sensitivity and reproducibility during the analytical procedure is recorded, the presence of a layer of surface oxides hinders the deposition of the analyte. The electrode was polished sequentially with suspensions of 1, 0.3, 0.05 μm alumina powder in HPW for 1 min, then WE was immersed three times into ethanol and water alternatively to remove the remaining $Al_2O_3$ particles from the surface.

**Table 3**
Electrochemical parameters characterising the DPASV method for determination of As(III).

| Pretreatment | Value |
|---|---|
| Purge time (s) | 300 |
| Stirring rate ($min^{-1}$) | 2000 |
| Conditioning potential (V) | 0.60 |
| Conditioning time (s) | 10 |
| Deposition potential (V) | −0.30 |
| Deposition time (s) | 50 |
| Equilibration time (s) | 10 |
| **Measurement** | |
| Modulation time (s) | 0.05 |
| Interval time (s) | 0.1 |
| **Potentials** | |
| Initial potential (V) | −0.20 |
| End potential (V) | 0.30 |
| Step potential (V) | 0.09 |
| Modulation amplitude (V) | 0.05 |

#### 2.3.2. Supporting electrolyte

Based on our previous study [29], the best electrolyte for the analytical procedure is 0.25 M HCl, which was found to be the medium that gives the strongest and clearest signals for the analyte, indicating that the charge transfer reactions at the active surface are fast and reversible. The As(III) compounds detectable in aqueous solutions containing HCl are $H_3AsO_3$, $As(OH)^{2+}$, $As(OH)_2Cl$, $As(OH)Cl_2$ and $AsCl_3$. Considering that $As(OH)_2Cl$ and $As(OH)Cl_2$ are believed to be the species actually involved in charge transfer reactions at the electrode [33, 34], an increase in HCl concentration improves the deposition efficiency of As(III). The choice of 0.25 M HCl rather than more concentrated solutions is a compromise between good analytical response and the need to maintain the repeatability of the technique and the stability of the active surface of the WE.

#### 2.3.3. DPASV procedure for selective As(III) determination

The supporting electrolyte adopted for the selective determination of As(III) consists of: 20 mL solution of 0.25 M HCl and 100 μL of $10^{-3}$ M ascorbic acid into the cell and purged with gaseous nitrogen for 300 s before the analyses. The removal of $O_2$ is significant in reducing the background currents, while it does not appear to affect the stability of the As peak. The optimized electrochemical parameters adopted for the analysis are reported in Table 3.

The reactions occurring at WE and CE during deposition are shown schematically below:

$$\text{WE: As(III)} + \text{Au} + H^+ + \Sigma(\text{Ox})_{imp} + ne^- \rightarrow As^0 + H_2 + \text{Au} + \Sigma(\text{Red})_{imp}$$

$$\text{CE: } 2Cl^- + \Sigma(\text{Red})_{imp} \rightarrow Cl_2 + \Sigma(\text{Ox})_{imp} + ne^- \rightarrow As^0 + H_2 + \text{Au} + \Sigma(\text{Red})_{imp}$$

$$(Cl_2)_g + H_2O \rightarrow HOCl + H^+ + Cl^-$$

where $\Sigma(\text{Ox})_{imp}$ and $\Sigma(\text{Red})_{imp}$ are traces of other substances that can be reduced or oxidised. The presence of an aliquot of ascorbic acid in solution acts to neutralise the effect of hypochlorous acid by converting it into dehydroascorbic acid and preventing the oxydation of As(III) to As (V) during the analyses:

$$As(OH)_3 + HOCl + \Sigma(\text{Ox})_{imp} \rightarrow OAs(OH)_3 + (Cl^-) + \Sigma(\text{Red})_{imp}$$

During this study, it was observed that the application of a conditioning potential could improve the quality and repeatability of the stripping peak [35]: an anodic potential restores the available surface area by bringing any remaining species adsorbed on the gold back into solution [36].

**Table 4**
Electrochemical parameters characterising the DPASV method for determination of As(III) + As(V).

| Pretreatment | Value |
|---|---|
| Purge time (s) | 300 |
| Stirring rate (rpm) | 2000 |
| Conditioning potential (V) | 0 |
| Conditioning time (s) | 0 |
| Deposition potential (V) | −1.20 |
| Deposition time (s) | 120 |
| Equilibration time (s) | 10 |
| **Measurement** | |
| Modulation time (s) | 0.05 |
| Interval time (s) | 0.1 |
| **Potentials** | |
| Initial potential (V) | −0.20 |
| End potential (V) | 0.30 |
| Step potential (V) | 0.09 |
| Modulation amplitude (V) | 0.05 |

#### 2.3.4. DPASV procedure for total inorganic As (As(III) + As(V)) determination

As(V) species are believed to be non-electroactive except under drastic conditions [5,17,37], so their reduction is required prior to the analyte deposition onto the working electrode. Various chemical reactants for inorganic As(V) reduction to As(III) are reported in literature: ascorbic acid, hydrazine hydrochloride, hydrazine sulphate [37], however only sodium sulphite was described as easy to implement and cost-effective. However, all these methods are not field amenable or not reproducible. Instead, this work investigated an electrochemical reduction method for As(V) compounds in solution by applying a high reducing potential.

The electrochemical reduction of the As(V) species present in solution and the deposition of $As^0$ on the active surface of the WE is achieved by the generation of hydrogen gas molecules on the active surface of WE, maintaining a deposition potential of −1.20 V for 120 s. However, $H_2$ formation on the active surface of the WE has the potential to prevent the deposition of the analyte and is therefore one of the main issues affecting the repeatability and reproducibility of the technique [5]. In this study, the effect of bubble formation during the deposition phase was mitigated by adopting a lateral SGE and a mild concentration of supporting electrolyte (0.25 M HCl). The choice of 0.25 M HCl is the result of a good compromise, as several experiments show the electro-inactivity of As(V) under weakly acidic conditions due to insufficient hydrogen formation [38]. The optimized parameters are reported in Table 4. The analysis yields total As; the contents of As(V) alone is evaluated indirectly by subtraction: As(V)=As(tot) - As(III). For speciation purposes it is not possible to include ascorbic acid as an antioxidant, since it would alter the distribution of the element between +3 and + 5 oxidation states.

## 3. Results and discussion

### 3.1. Method characterization

#### 3.1.1. Effect of deposition time variation on peak intensity and measurement repeatability for As (III)

The choice of the deposition time was made considering the concentration of the analyte in question; the literature suggests times ranging from 30 s for concentrations around $\sim 10^{-7}$ M to 20 min for concentrations of $10^{-10}$ M [32]. Given that arsenic concentrations in water are generally between 0.1 and 10 μg $L^{-1}$ [3], i.e. $10^{-7} - 10^{-9}$ M. A deposition time of 50 s was selected. As shown in Fig. S3, the difference in analytical responses was evaluated by performing an analysis on 5 μg $L^{-1}$ of As(III) using various deposition times (15, 30, 50, 75, 100, 150, and 200 s).

According to Faraday's law, the concentration of the analyte at the active surface of WE is proportional to the deposition time, which affects the sensitivity of the analytical response by producing higher peak currents at longer deposition times. It is observed that beyond 150 s of deposition, the signal intensity reaches a plateau, making further prolongation of analysis times ineffective. Despite an improvement in sensitivity, a comparison between depositions of 50 and 100 s showed that reducing the deposition time allows for an extension of the linear range and improves the repeatability of the analytical response. This occurs because, with increased deposition time, non-conductive $As^0$ coatings can form and deposit on the electrode surface.

#### 3.1.2. Linear range

The evaluation of the linearity of the instrumental response as a function of analyte concentration is essential for conducting quantitative studies. The slope (m), intercept (q), and the coefficient of determination ($R^2$) were used to draw conclusions on this matter. Additionally, percentage recoveries were calculated: assuming the first addition represented an unknown sample, its concentration was evaluated based on the signals from subsequent additions using the standard additions method. The recoveries, calculated as the ratio between the calculated and expected concentration, multiplied by 100 $\left[\left(\frac{[As]\ calculated}{[As]\ expected}\right)x100\right]$, yielded satisfactory results for all case studies (Table S1) [39].

During the method optimization phase for monitoring As(III), concentration ranges between 50 % and 150 % of the expected concentration value (i.e. the concentration of the first spike) were evaluated. Considering the legislative limit for drinking water is 10 μg $L^{-1}$, and the average total arsenic concentrations in aquatic systems range between 0.1 and 10 μg $L^{-1}$ [28], the linearity of the response was investigated in the following ranges for As(III): 0.5–2.5 μg $L^{-1}$, 1–5 μg $L^{-1}$, 2–10 μg $L^{-1}$. Fig. S4 shows the voltammograms recorded for 1–5 μg $L^{-1}$ As (III). The relationship between the amount of As in solution and the analytical signal was also evaluated for As(V) species (Table S2 and Fig. S5). It can be stated that the results obtained demonstrate the existence of a linear relationship between the analyte concentration and the instrumental response; therefore, they can be considered satisfactory, especially when considering the low concentrations present in the system. In all cases, the percentage recoveries for the first addition do not exceed 115 %. The sensitivity of a method indicates how responsive it is to changes in analyte concentration and can be assessed by considering the slope of the calibration curve [39]. For both As(III) and As(V), it is observed that the latter decreases as the concentrations increase, with one exception: this trend is typical of voltammetry and indicates that the deposition efficiency is better at lower concentrations, due to reduced competition among the analytes for space on the electrode surface [39].

#### 3.1.3. Repeatability: intercell and intracell

Repeatability is considered satisfactory if the frequency of random errors is negligible and if fluctuations in the analytical responses do not exceed 5 %. The repeatability of the techniques developed for the determination of As(III) and total As by performing five consecutive measurements of solutions containing known concentrations of the analyte. Repeatability was assessed both by recording sequential scans within the same cell (intracell) and by preparing a new solution for each measurement (intercell). The results obtained for the As(III) method are illustrated in Table S3. On the other hand, in the results recorded for $As_{tot}$, the difference in terms of RSD% among repeated measurements in the two modes was outstanding: RSD% reported in Table S4 proves that the instrumental signal decays quite rapidly after a repeated series of analyses carried out on the same solution. The strongly reducing conditions in which the analyte is deposited, the formation of $H_2$ at the WE and $Cl_2$ at the CE, was considered as the cause of the instability observed in a repeated series of scans and as the main problem affecting the repeatability of the technique.

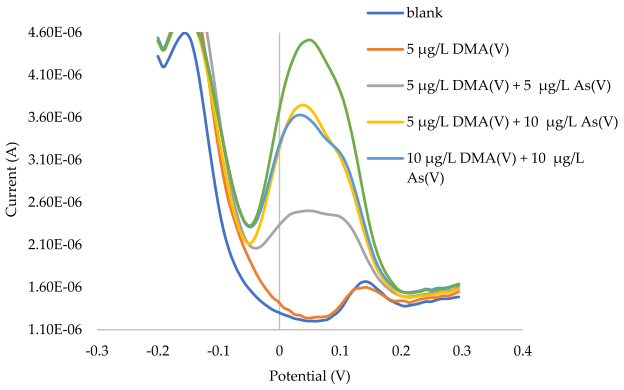


**Fig. 1.** The voltammogram shows that there are no changes in the inorganic As (V) signals in the presence of increasing concentrations of DMAs.

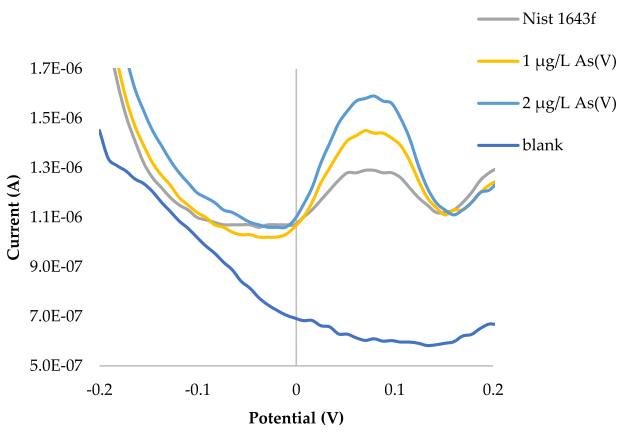


**Fig. 2.** Voltammogram of the determination of As in Nist 1643f.

### 3.1.4. Accuracy

The accuracy of the procedure was tested by analysing solutions containing known concentrations of As(III) and As(total) and computing the recovery% compared to the added quantity. At first, the accuracy for As(III) method was investigated by preparing solutions containing an aliquot of 0.5 M HCl (10 mL) and an aliquot of HPW (10 mL) added with 1.0 and 2.5 µg $L^{-1}$ of As(III). Then, the test was carried out on a sample of tap water taken from the laboratory sink with 1.0 and 2.0 µg $L^{-1}$ of As (III). The accuracy for the total inorganic As was assessed by preparing a solution of HPW added with 3 µg $L^{-1}$ of As(III) and 3 µg $L^{-1}$ of As(V). Then, As(V) concentration alone was determined by subtraction (see 2.3.4). All analyses were performed in duplicate. Results are shown in Tables S5–S6 and Figs. S6–S7.

## 3.2. Interferences

### 3.2.1. Metals

The interference of several metal ions, namely Cd(II), Co(II); Cr(III), Cu(II), Fe(III), Hg(II), Mn(II), Ni(II) and Pb(II) on the arsenic stripping signal was investigated. The voltammogram of a solution with 5 µg $L^{-1}$ of As(V) was recorded in the presence of each element (added into the cell in 1:1, 1:10, 1:100 concentration ratios with respect to As(V)). As other researchers [5,22,34] found, no interference was observed after the addition of 500 µg $L^{-1}$ of Cd, Co, Cr, Fe. On the other hand, the presence of 500 µg $L^{-1}$ of Mn and Ni in solution was found to reduce the analytical signal by 12 % and 28 %, respectively. The effect of the co-presence of As and Mn resulted in an interference caused by the formation of an unusual redox couple between As(V) and $Mn^0$. During the deposition step at −1.2 V, Mn(II) in solution competes for the active sites of gold and is deposited on the electrode as $Mn^0$, thus depriving the arsenic of part of the available WE surface area [38]. Pb, Hg and Cu showed a greater influence on the analytical signals of As. Tests showed a 40 % decrease in the intensity of As peak in the presence of 50 µg $L^{-1}$ Pb, a 6 % and 15 % decrease of peak height in the presence of 5 and 50 µg $L^{-1}$ Hg and a 20 % and 30 % decrease in the presence of 5 and 50 µg $L^{-1}$ of Cu. When the solution contained 500 µg $L^{-1}$ of each interfering species, no As(V) peak was observed. Pb and Hg compete with As for active sites on the surface of the working electrode without forming intermetallic compounds [37]; both metal ions are deposited together with arsenic at a deposition potential of −1.20 V and show analytical signals at −0.20 V (Pb) and +0.50 V (Hg). Copper is the interfering ion that showed the most detrimental effect on the As stripping signal due to co-deposition with As on the active Au electrode surface [40] ands to the formation of intermetallic compounds with different stoichiometric ratios ($Cu_xAs_y$) [41]. The percentage of recovery of As(V) obtained in presence of various concentrations of potentially interfering metal ions are shown in Fig. S8.

### 3.2.2. Organic arsenic

In organic form, As can occur in environmental aquatic systems in a variety of organoarsenic compounds, but mainly as monomethylarsonic acid (MMA(V)), dimethylarsonic (cacodylic) acid (DMA(V)) and trimethylarsine oxide (TMAsO). The formation and subsequent concentration of methylated As(V) species in aquatic systems depends mainly on biological processes: microorganisms in the photic zone of natural waters can methylate inorganic As compounds and convert them to MMA(V), DMA(V) and TMAsO under oxidising conditions [42]. Inorganic arsenic forms are thought to be at least ten times more abundant, toxic and mobile than MMA(V) and DMA(V) [5]. As other researchers found [22, 33], in this work it was assessed that organo-arsenic compounds are not electroactive and that further additions of DMA(V) do not interfere with the growth of the analytical peak for 5 µg $L^{-1}$ of inorganic As(V) (Fig. 1).

## 3.3. Application of the method on real samples

### 3.3.1. Standard reference materials (SRM)

The accuracy of the voltammetric method, already demonstrated in synthetic solutions (see chapter 3.1.4), was assessed through the analysis of NIST SRM 1643f "*Trace Elements in Water*," which is generally used to evaluate procedures aimed at determining trace elements present in natural waters. The DPASV voltammetric analysis was conducted for the determination of both As(III) and As(V); however, as no analytical response was observed for As(III), it was concluded that As was present in the sample as As(V). Given the certified concentration of As(V) of 57.42 ± 0.38 µg $L^{-1}$, the voltammetric analysis was performed by preparing a cell containing 0.5 mL of the sample and 19.5 mL of 0.25 M HCl. A dilution factor of 40 was considered in the calculation of the final concentration.

Fig. 2 shows the voltammograms recorded during the test. The results confirmed the good accuracy of the method (54.39 ± 0.71 µg $L^{-1}$, 94.7 % recovery), which was then applied to the analysis of various kinds of water.

### 3.3.2. Water samples

The voltammetric analysis of real water samples was performed in duplicate and the voltammetric cell was composed by an aliquot of the sample (10 mL) diluted 1:1 with the supporting electrolyte (0.50 M HCl). The experimental results are summarised in Table S7, voltammogram referred to the water samples are reported in Figs. S9–S14.

All samples showed concentrations of total inorganic As below 10 µg $L^{-1}$, the limit recommended by WHO. Only two samples, TH-1 and TH-2, showed detectable concentrations of arsenites. These are the only two saline waters analysed during the study. High salinity can reduce the solubility of gases such as $O_2$, affecting oxidation-reduction processes

**Table 5**
As concentration obtained from water samples analysis performed by HG-ICP-OES method and percentage difference with DPASV results.

| | DPASV | | HG-ICP-OES | | Difference % |
|---|---|---|---|---|---|
| Sample name | As(tot) (μg $L^{-1}$) | RSD % | As(tot) μg $L^{-1}$ | RSD % | |
| IT-1 | < LOD | | <LOD | | |
| IT-2 | 0.49 ± 0.01 | 2.01 | 0.60 ± 0.02 | 5.95 | −18 |
| IT-3 | 0.40 ± 0.02 | 5.65 | <LOD | | |
| IT-4 | 1.53 ± 0.01 | 0.37 | 1.30 ± 0.3 | 20.0 | 17.0 |
| DEN | 8.10 ± 0.70 | 8.68 | 8.24 ± 0.02 | 0.40 | −1.7 |
| TH-1 | 8.00 ± 0.60 | 7.10 | 7.84 ± 0.05 | 0.65 | 2.0 |
| TH-2 | 5.34 ± 0.04 | 0.69 | 6.26 ± 0.04 | 0.56 | −14.7 |
| TH-3 | 1.95 ± 0.03 | 1.45 | 1.18 ± 0.01 | 0.83 | 65 |
| TH-4 | 4.50 ± 0.5 | 11.7 | 4.71 ± 0.05 | 1.07 | −4.4 |

*tap water samples were collected on two different dates: April 11, 2024 for DPASV and May 03, 2024 for HG-ICP-OES analysis

and stabilising As(III) compounds in solution.

### 3.3.3. Comparison with HG-ICP-OES

As concentrations determined in the real samples using the DPASV voltammetric method were compared with those obtained by HG-ICP-OES, in order to verify the reliability of the results obtained. The experimental results obtained with the two techniques showed satisfactory agreement, as no significant differences were observed. HG-ICP-OES confirmed that no sample exceeded the recommended limit (10 μg $L^{-1}$). The percentage difference between the experimental results was calculated as follows: $\left[\left(\frac{[As]DPASV-[As]HG-ICP-OES}{[As]HG-ICP-OES}\right)x100\right]$

The results obtained by HG-ICP-OES are shown in Table 5.

A paired *t*-test was performed to check whether or not the results obtained with the methods used for the determination of As within the water samples were significantly different. The paired *t*-test is a test of accuracy, applied in attendance of *n* different samples on which measurements were performed with two different methods. A 95 % confidence interval (α = 0,05) was selected for the two-tailed *t*-test, showing that there was no significant difference between the results obtained using DPASV and those obtained by HG-ICP-OES methods (Table S8).

### 3.4. Application on portable analyzer

The analytical procedure for on-site monitoring of As with a portable analyzer was characterized by evaluating parameters such as sensitivity, linearity, and repeatability, and comparing these results with data obtained using a laboratory potentiostat. The following concentration ranges were investigated for the determination of As(III) and As(V): 2–10 μg $L^{-1}$ and 5–25 μg $L^{-1}$. Table S9 shows the determination coefficients and % recoveries obtained by quantifying the concentrations of the first addition during linearity tests for the As(III) and As(V) methods.

Fig. S15 shows the voltammogram obtained for five successive additions of As(III) while Fig. S16 displays the voltammogram obtained for five successive additions of As(V). A satisfactory linearity was observed, with higher $R^2$ values for As(III) than for As(V). The sensitivity of the measurements with the portable analyzer was lower than with the laboratory one, due to the lower stirring rate achieved with the magnetic stirrer connected to the former, in comparison to the stirring engine mounted on the laboratory stand: the mass transport, and consequently the amount of analyte deposited onto the electrode during the deposition step, is lower. The availability of a portable engine would allow an increase in the sensitivity.

The repeatability of the technique was evaluated by analyzing solutions containing 20 mL of 0.25 M HCl and 5 μg $L^{-1}$ of analyte (Table S10). Both 5 successive analyses on the same solution and 5 consecutive analyses with a freshly prepared cell containing the same analyte concentration were performed to value intracell and intercell repeatability, respectively.

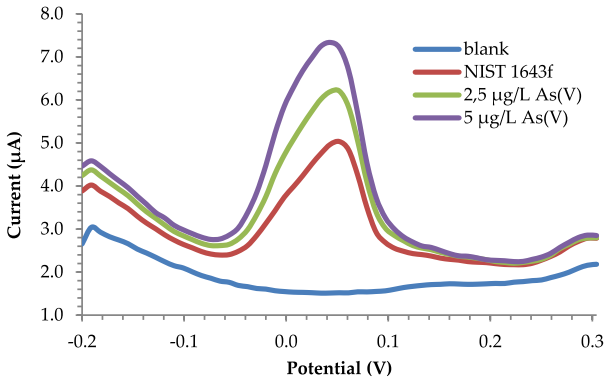


**Fig. 3.** Voltammogram regarding NIST 1643 analized with portable instrument.

**Table 6**
Comparison between portable and laboratory instrumentation.

| Sample ID | [As(tot)] Palmsens μg $L^{-1}$ | RSD % | [As(tot)] Autolab | RSD % | Difference % |
|---|---|---|---|---|---|
| TH-1 | 7.39 ± 0.44 | 6.01 | 7.98 ± 0.57 | 7.1 | −7.9 |
| TH-2 | 5.09 ± 0.28 | 5.51 | 5.34 ± 0.04 | 0.69 | −4.9 |
| TH-4 | 3.80 ± 0.50 | 13.1 | 4.55 ± 0.53 | 11.7 | −19 % |

The repeatability data obtained are in good agreement with those previously observed with the laboratory instrument. However, it is noteworthy that there is no progressive decrease in the analytical signal during the assessment of intracell repeatability for solutions containing 5 μg $L^{-1}$ of As(V). Similarly to the characterization phase of the electrochemical technique, the accuracy of the method for As determination using portable instrumentation was evaluated by considering the percentage recovery relative to the concentration provided by a certified reference material NIST 1643f '*Trace Elements in Water*.' The measurement system consists of 0.5 mL of SRM and 19.5 mL of 0.25 M HCl; the concentration of As calculated by portable voltammetry is compared with the certified value, a satisfactory agreement (62.85 ± 1.14 μg $L^{-1}$, 109 % recovery) is observed, confirming the accuracy of the method. Fig. 3 presents the voltammogram recorded during the test.

To facilitate a comparison of the applicability of the voltammetric method using a portable potentiostat versus a laboratory potentiostat, several samples were analysed. Given the lower sensitivity observed with the portable instrumentation and the concentration of As detected in the available real samples, the concentration of total As was monitored in water samples from Thailand labelled TH-1, TH-2, TH-4. It is worth noting that it was not possible to detect measurable analytical peaks in some samples where the As concentration obtained with the laboratory instrument was below 1 μg $L^{-1}$. Table 6 and Fig. 4 presents a comparison of the total As concentrations obtained using the portable Palmsens4 potentiostat and the laboratory Autolab PGSTAT10 potentiostat.

The obtained results also shown in terms of percentage difference in concentration, are consistent and deemed satisfactory, especially considering the low concentrations involved. The entire procedure for the determination of a field sample takes approximately 15 min, making the technique suitable for routine analyses. Compared to analyses performed using conventional techniques, this method requires less expensive instrumentation and significantly reduces the use of gases and solvents. Additionally, the whole setup is highly compact and easy to use, also for not specialized operators.

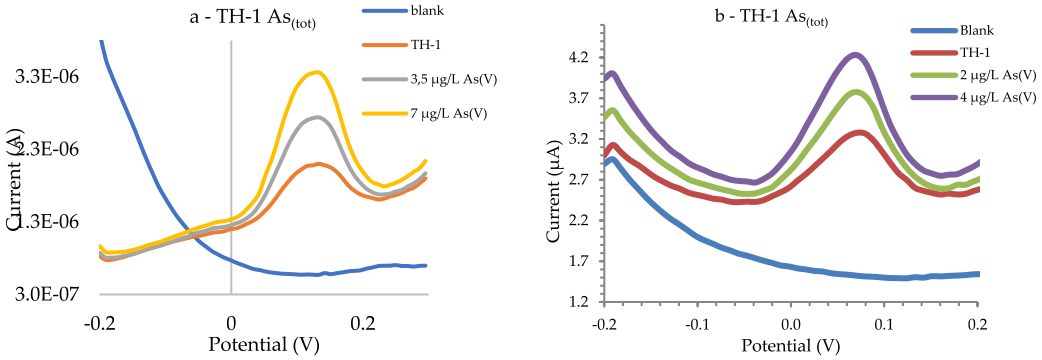


**Fig. 4.** – Voltammogram of As(tot) in sample TH-1 with laboratory procedure (a) and portable procedure (b).

## 4. Conclusions

The result obtained showed the efficiency of the method developed for the determination of low concentrations of total inorganic As and for speciation analyses aimed at distinguishing inorganic As compounds with oxidation state +3 and + 5. We demonstrated that an electrochemical reduction of As(V) compounds is possible under pronouncedly reduction conditions, giving the DPASV method some interesting advantages in terms of shorter analysis time compared to chemical reduction procedures, the decrease in consumption of chemical reagents, the ability to perform real-time monitoring and on-site analysis. The method was characterised in terms of linearity, repeatability and accuracy with satisfactory results. The DPASV method was therefore applied to the determination and speciation of As in real water samples after the development and optimization phase; all samples analysed showed concentrations of total inorganic As below 10 µg $L^{-1}$. In two of the samples analysed it was possible distinguish between As(III) and As (V) compounds, whereas only As(V) was detected in the other samples. The voltammetric method yielded similar results to the HG-ICP-OES technique, but it has some advantages: lower analysis costs, relatively shorter analysis times (if a limited number of samples is processed) and the ability to perform speciation analysis. In the final stages of this study, the developed voltammetric method was applied to a portable potentiostat in order to test the actual possibility of carrying out on-site analysis. Again, the results are consistent with those obtained by laboratory potentiostat and HG-ICP-OES spectroscopy and the portable potentiostat was successfully tested in on-site analysis.

## CRediT authorship contribution statement

**Paolo Inaudi:** Writing – original draft, Supervision, Investigation, Data curation. **Christian Esposito:** Writing – original draft, Validation, Investigation. **Mery Malandrino:** Writing – review & editing. **Laura Favilli:** Writing – review & editing. **Agnese Giacomino:** Visualization, Funding acquisition. **Ornella Abollino:** Supervision, Conceptualization.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2025.127880.

## Data availability

No data was used for the research described in the article.

## References

[1] K.R. Henke, Arsenic: Environmental Chemistry, Health Threats and Waste Treatments, Wiley Publications, New York, 2009.
[2] A.L. Foster, Spectroscopic investigations of arsenic species in solid phases, in: A. H. Welch, K.G. Stollenwerk (Eds.), Arsenic in Groundwater, Springer, Boston, MA, 2003, pp. 27–65, https://doi.org/10.1007/0-306-47956-7_2.
[3] M. Moats, L. Alagha, K. Awuah-Offei, Towards resilient and sustainable supply of critical elements from the copper supply chain: a review, J. Clean. Prod. 307 (2021) 2–15, https://doi.org/10.1016/j.jclepro.2021.127207.
[4] A.D. Redman, D.L. Macalady, D. Ahmann, Natural organic matter affects arsenic speciation and sorption onto hematite, Environmental Science and Technolgy 32 (2002) 2889–2896, https://doi.org/10.1021/es0112801.
[5] P. Salaun, B. Planer-Friederich, C.M.G. Van den Berg, Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode, Anal. Chim. Acta 585 (2007) 312–322, https://doi.org/10.1016/j.aca.2006.12.048, 2007.
[6] R.J. Bowell, C.N. Alpers, H.E. Jamieson, D.K. Nordstrom, Arsenic environmental mineralogy and microbiology, Rev. Mineral. Geochem. 79 (2015) 1–204.
[7] A.P. Singh, R.K. Goel, T. Kaur, Mechanisms pertaining to arsenic toxicity, Toxicol. Int. 18 (2011) 87–93, https://doi.org/10.4103/0971-6580.84258.
[8] Md S. Rahaman, MdM. Rahman, N. Mise, Md T. Sikder, G. Ichihara, Md K. Uddin, M. Kurasaki, S. Ichihara, Environmental arsenic exposure and its contribution to human diseases, toxicity mechanism and management, Environ. Pollut. 289 (2021) 1–11, https://doi.org/10.1016/j.envpol.2021.117940.
[9] WHO, Guidelines for Drinking-Water Quality, fourth ed., 2022 with 1st and 2nd addendum.
[10] H.Md Anawar, Arsenic speciation in environmental samples by hydride generation and electrothermal atomic absorption spectrometry, Talanta 88 (2012) 30–42, https://doi.org/10.1016/j.talanta.2011.11.068.
[11] M. Welna, A. Szymczycha-Madeja, P. Pohl, Improvement of determination of trace amounts of arsenic and selenium in slim coffee products by HG-ICP-OES, Food Anal. Methods 7 (2014) 1016–1023, https://doi.org/10.1007/s12161-013-9707-4.
[12] B. Chen, M. Krachler, Z.I. Gonzalez, W. Shotyk, Improved determination of arsenic in environmental and geological specimens using HG-AFS, J. Anal. Atomic Spectrom. 20 (2005) 95–102, https://doi.org/10.1039/B416142D.
[13] Á.H. Pétursdóttir, N. Friedrich, S. Musil, A. Raab, H. Gunnlaugsdóttir, E.M. Krupp, J. Feldmann, Hydride generation ICP-MS as a simple method for determination of inorganic arsenic in rice for routine biomonitoring, Anal. Methods 6 (2014) 5392–5396, https://doi.org/10.1039/C4AY00423J.
[14] E.A. Serban, G.G. Vasile, T. Galaon, C. Ena, L.F. Pascu, HG-ICP-OES technique, a useful tool for arsenic determination in soft water, Revista de Chemie 71 (2020) 379–390, https://doi.org/10.37358/RC.20.7.8255.

[15] Z.G. Liu, X.J. Huang, Voltammetric determination of inorganic arsenic, Trends Anal. Chem. 60 (2014) 25–35, https://doi.org/10.1016/j.trac.2014.04.014.
[16] B. Radke, L. Jewell, J. Namieśnik, Analysis of arsenic species in environmental samples, Crit. Rev. Anal. Chem. 42 (2012) 162–283, https://doi.org/10.1080/10408347.2011.634637.
[17] D.E. Mays, A. Hussam, Voltammetric methods for determination and speciation of inorganic arsenic in the environment - a review, Anal. Chim. Acta 646 (2009) 6–16, https://doi.org/10.1016/j.aca.2009.05.006.
[18] E. Majid, S. Hrapovic, Y. Liu, K.B. Male, J.H.T. Luong, Electrochemical determination of arsenite using a gold nanoparticle modified glassy carbon electrode and flow analysis, Anal. Chem. 78 (2006) 762–769, https://doi.org/10.1021/ac0513562.
[19] Y. Zhang, D. Li, R.G. Compton, Arsenic (III) detection with underpotential deposition and anodic stripping voltammetry, Chemelectrochem 8 (2021) 3707–3715, https://doi.org/10.1002/celc.202101022.
[20] M. Hossain, Md M. Islam, S. Ferdousi, T. Okajima, T. Osaka, Anodic stripping voltammetry detection of arsenic(III) at gold nanoparticle-modified glassy carbon electrodes prepared by electrodeposition in the presence of various additives, Electroanalysis, 20, pp. 2435-2441, https://doi.org/10.1002/elan.200804339;.
[21] L.Y. Martynov, A.V. Dymova, I.A. Semyachkin, A.V. Nukulin, K.A. Sakharov, N. A. Yashtulov, N.K. Zaytsev, Electrochemical and microscopic study of a rotating disk Gold-Film electrode for voltammetric determination of arsenic (III), Microchem. J. 205 (2024) 1–10, https://doi.org/10.1016/j.microc.2024.111177.
[22] K. Gibbon-Walsh, P. Salaun, C.M.G. van den Berg, Determination of arsenate in natural pH seawater using a manganese-coated gold microwire electrode, Anal. Chim. Acta 710 (2012) 50–57, https://doi.org/10.1016/j.aca.2011.10.041.
[23] E.A. Zakharova, G.N. Noskova, A.S. Kabakaev, N.V. Rees, R.G. Compton, Gold microelectrodes ensembles; cheap, reusable, and stable electrodes for determination of arsenic (V) under aerobic conditions, pp. 1105–1115, https://doi.org/10.1080/03067319.2012.690151, 2013.
[24] Y. Song, G.M. Swain, Total inorganic arsenic detection in real water samples using anodic stripping voltammetry and a gold coated diamond thin-film electrode, Anal. Chim. Acta 593 (2007) 7–12, https://doi.org/10.1016/j.aca.2007.04.033.
[25] M. Khairy, D.K. Kamporius, R.O. Kadara, C.E. Banks, Gold nanoparticle modified screen printed electrodes for the trace sensing of arsenic (III) in the presence of copper (III), Electroanalysis 22 (2010) 2496–2501, https://doi.org/10.1002/elan.201000226.
[26] L. Xiao, G.G. Wildgoose, R.G. Compton, Sensitive electrochemical detection of arsenic (III) using gold nanoparticle modified carbon nanotubes via anodic stripping voltammetry, Anal. Chim. Acta 620 (2008) 44–49, https://doi.org/10.1016/j.aca.2008.05.015.
[27] D. Li, J. Li, X. Jia, Y. Han, E. Wang, Electrochemical determination of arsenic (III) on mercaptoethylamine modified Au electrode in neutral media, Anal. Chim. Acta 773 (2012) 23–27, https://doi.org/10.1016/j.aca.2012.04.030.
[28] A.R. Kumar, P. Riyazuddin, Preservation of inorganic arsenic species in environmental water samples for reliable speciation analysis, Trends Anal. Chem. 29 (2010) 1212–1222, https://doi.org/10.1016/j.trac.2010.07.009.
[29] A. Giacomino, O. Abollino, M. Lazzara, M. Malandrino, E. Mentasti, Determination of As(III) by anodic stripping voltammetry using a lateral gold electrode: experimental conditions, electron transfer and monitoring of electrode surface, Talanta 83 (2011) 1428–1435, https://doi.org/10.1016/j.talanta.2010.11.033.
[30] S. Yilmaz, B. Baba, A. Baba, S. Yagmur, M. Citak, Direct quantitative determination of total arsenic in natural hotwaters by anodic stripping voltammetry at the rotating lateral gold electrode, Curr. Anal. Chem. 5 (2009) 29–34, https://doi.org/10.2174/157341109787047934.
[31] N. Dirilgen, F. Dogan, H. Ozbal, Anodic stripping voltammetry: arsenic determination in ancient bone samples, Anal. Lett. 39 (2006) 127–143, https://doi.org/10.1080/00032710500464264.
[32] J. Wang, Analytical Electrochemistry, third ed., Wiley-VCH publisher, 2006.
[33] K. Gibbon-Walsh, P. Salaun, C.M.G. Van den Berg, Arsenic speciation in natural waters by cathodic stripping voltammetry, Anal. Chim. Acta 662 (2010) 1–8, https://doi.org/10.1016/j.aca.2009.12.038.
[34] E. Muñoz, S. Palmero, Analysis and speciation of arsenic by stripping potentiometry: a review, Talanta, 65, pp. 613-620, https://doi.org/10.1016/j.talanta.2004.07.034;.
[35] Y.C. Sun, J. Mierzwa, M.H. Yang, New method of gold-film electrode preparation for anodic stripping voltametric determination of arsenic (III and V) in seawater, Talanta 44 (1997) 1379–1387, https://doi.org/10.1016/S0039-9140(96)02197-2.
[36] A. Alispahic, A. Krivohlavek, N. Galic, Novel preservation method for inorganic arsenic speciation in model and natural water samples by stripping voltammetric method, Appl. Sci. 11 (2021) 1–14, https://doi.org/10.3390/app11198811.
[37] R. Feeney, S.P. Kounaves, Voltammetric measurement of arsenic in natural waters, Talanta 58 (2002) 23–31, https://doi.org/10.1016/S0039-9140(02)00253-9.
[38] K. Gibbon-Walsh, P. Salaun, C.M.G. Van den Berg, Arsenic speciation in natural waters by cathodic stripping voltammetry, Anal. Chim. Acta 662 (2010) 1–8, https://doi.org/10.1016/j.aca.2009.12.038.
[39] S.A. Ozkan, Electroanalytical Methods in Pharmaceutical Analysis and Their Validation, HNB Publishing, 2012.
[40] X. Dai, R.G. Compton, Gold nanoparticle modified electrodes show a reduced interference by Cu(II) in the detection of as(III) using anodic stripping voltammetry, Electroanalysis 17 (2005) 1325–1330, https://doi.org/10.1002/elan.200403246, 2005.
[41] A. Profumo, D. Merli, M. Pesavento, Voltammetric determination of inorganic As (III) and total inorganic as in natural waters, Anal. Chim. Acta 539 (2005) 245–250, https://doi.org/10.1016/j.aca.2005.02.062.
[42] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, Talanta 58 (2002) 201–235, https://doi.org/10.1016/S0039-9140(02)00268-0.