



Inorganic arsenic speciation by electroanalysis. From laboratory to field conditions: A mini-review



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ABSTRACT

The accurate on-site monitoring of arsenic in water is still an important issue for many countries. This review considers the most promising electrochemical methods for the analysis and speciation of the inorganic forms of arsenic under field conditions, with an emphasis on stripping voltammetry.

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1. Introduction

Environmental monitoring of arsenic in water has attracted much scientific attention as arsenic contamination of drinking water poses a major danger to human life and health. About 200 million people in 70 countries are at risk of poisoning by drinking water contaminated with arsenic, which can cause a range of adverse health effects including serious chronic diseases and even death [1,2]. The World Health Organization (WHO) recommended that the maximum allowable concentration for As in drinking water should be lowered from 200 ppb in 1958 to 50 ppb in 1963, and this figure was reduced again to 10 ppb in 1993 based on concerns regarding its carcinogenicity in humans [3]. This has made it difficult to analyze samples on site because the existing test kits have not been sufficiently sensitive [4,5]. Laboratory methods, on the other hand, are expensive, non-portable and often require sample preparation which could lead to the transformation of arsenic between its different forms [4,6–8] – and it is known that the form of the arsenic present has an influence on its migration, bioavailability and toxicity [1]. In recent times electrochemical methods have been shown to be successful for on-site detection of arsenic due to the portability and low cost of the equipment as well as the sensitivity and specificity of the techniques, especially in the detection of the toxic As(III) form [4,7,9–11].

According to the CAPLUS database, over the last twenty-five years there have been >100 reviews on various aspects of As speciation. Eight of these reviews highlighted electrochemical methods as the most suitable approach for field analysis [9–11]. The main topics

covered by some of these reviews are summarized below. Reviews [1, 12] give the regulations for the levels of As concentration permitted in different samples and the list of certified reference materials for arsenic [6]. Other reviews consider the special features of As and its species determination by a variety of techniques [6–8,13–15] including voltammetric methods [9], as well as various combined techniques of which HPLC-ICPMS is the most powerful [6,14,15]. Critical overviews of review articles dealing with As speciation are given in [14,16].

Inorganic and organic As compounds and their chemical transformations and toxicity are covered in articles [1,8,12,14,17,18] while the electrochemical behavior of As in solution is considered in reviews [9,10,11, 19].

The substantial works [6,8,9,14,20] cover in detail the analysis of various real samples, procedures for sampling, storage and sample preparation, including the possibility of separating and concentrating different As forms. The various electrochemical techniques (voltammetry [9–11] and potentiometry [19], flow and amperometric methods), modes, and As speciation conditions [10], applied electrodes [10,11], electrode materials and their modification [11,18,21], biosensors [11, 22], background electrolytes [19] as well as the measurement of parameters such as the limit of detection (LOD), linear range and sensitivity are summarized in reviews [9–11].

The articles by Melamed and Yogarajah et al. describe the test kits available for As determination and the characteristics of an ideal, routine arsenic sensor for field analysis combined with a microfluidic system for on-line monitoring of As levels [4,5].

In view of the huge amount of information available on arsenic analysis, this mini-review will be limited to the problem of inorganic As speciation analysis in water, in particular focusing on methods using anodic stripping voltammetry (ASV). We will consider: 1) ASV methods with

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gold microelectrodes for As(III) determination in natural or alkaline media; 2) issues related to As(V) determination; 3) direct and indirect methods for As speciation using voltammetry, and the prospect of using these methods in the field.

2. As(III) determination by anodic stripping voltammetry (ASV)

Of the two forms of As(III) and (V), only the arsenite is selectively determined over a wide pH range on gold electrodes by ASV. Procedures for its determination at the ppb level in an acid medium are well documented and standardized (see, for example, USEPA [23], Russian GOST [24]). H_3AsO_3 is usually pre-concentrated on the electrodes in the form of As(0) and then an anodic scan of the potential is carried out in linear sweep (LSV), square wave (SWV) and differential pulse (DPV) modes. The signal of As(0 \rightarrow 3) is registered and its height is proportional to the As(III) concentration, with E_p dependent on the pH of the solution.

Sometimes the second anodic As(3 \rightarrow 5) peak is fixed following the first anodic one; it is less sensitive but more specific [25–29]. A second peak could be registered on Pt, Ir, IrO_x , or CoO_x electrodes due to catalytic processes [30–35]. A great amount of work has been done with acid (HCl) backgrounds, where the As(III) form is unstable, making speciation analysis difficult. Below we look at some research directions for As speciation analysis in the field using ASV.

- (1) There are numerous publications which describe As(III) detection at low LOD (calculated by 3σ crit.). For example, LODs in the range 0.01–0.05 ppb are presented in [26,36–42] and LOD lower than 0.005 ppb in [43–48]. A number of different approaches have been used to improve the sensitivity of detection:
 - (i) Modification of electrodes using ensembles of metal nanoparticles (M-NPs) ([9,11,21,37] and refs. therein) and composites (M-NPs with carbon nanotubes or graphene) with electrocatalytic and adsorption properties [28,46,49–54,55–63].
 - (ii) Developing surfaces with specific morphology [45,56,64–70].
 - (iii) By double concentration [71], reinforced mass transfer [72–74] or rapid voltage scanning [28,29,75].
- (2) The specificity (selectivity) of As determination can be enhanced by decreasing the interference of solution components such as copper and surfactants [76]. This may be done by changing the composition of the background solutions [48,77] and the measured signal (As 3 \rightarrow 5); or by modifying the surface using M-NPs, their composites [37,51,58,78–80], ligands ($-\text{SH}$, $-\text{NH}_2$) or organic membranes [11,38,40,44,49,56,80,81]. Other effective methods employ flow-through systems [82] or cation exchangers [43,75,83–86].
- (3) There is a tendency to use natural or alkaline media to speciate As in real water to prevent conversion of the As(III) form and to exclude the need for sample preparation [25,26,40,57,86–94].
- (4) Methods used to increase the reproducibility and working life of electrodes include electrochemical pretreatment of the surface, renewal of the working layer [4,26,95] as well as use of screen-printed electrodes which can be replaced cheaply [80,96–98].
- (5) The analysis can be simplified by: the replacement of precious metal electrodes by inexpensive materials [44,47,33,60,99–104]; analysis without removing oxygen from solution [38,55,75,91]; minimizing the sample preparation stage by eliminating the reduction of As(V) to As(III), and speciation of As in the field. Automation of procedures is helpful and there has been some research aimed at creating microfluidic total analysis systems which would be ideal for this purpose [4].

Overall, more than eighty articles [14] dealing with new chemical or bio-sensors for As(III) detection with sufficient sensitivity or specificity are published every year. However, they rarely mention electrode

lifetime, robustness (although this was done in [105,106]), surface renewal methods, or ease of manufacturing, all of which are essential for speciation analysis in the field. This may well explain why we found that there are relatively few examples of electrochemical analyzers suitable for on-site analysis in the literature [21,36,96,107–112].

3. Determination of As(V)

For many years the As(V) signal was not obtained using anodic stripping voltammetry but rather determined indirectly. Since discharge of arsenite (3 \rightarrow 0) occurs easily on many electrodes it can be confused by kinetic difficulties with the step As(V) \rightarrow As(III). Currently the signal from As(V) in solution is obtained after electrolysis with Au electrodes, following anodic potential sweep (LSV or SWV) as the result of the reaction As(0) \rightarrow As(III) under the conditions presented in Table 1.

This signal (as a peak) coincides with that of As(III) and depends on the same factors (C_{As} , pH, potential sweep rate, etc.). However under the same conditions the accumulated amount of As(V) is less than the amount of As(III), therefore the sensitivity of As(V) detection is 2–4 times lower.

It can be seen from Table 1 that the use of microelectrodes, or their arrays, high negative potential, an acidic medium or heating of the electrode are necessary conditions for As(V) accumulation on the electrodes. The vibration of the electrode resulted in the removal of the hydrogen bubbles hindering analysis. Gibbon-Welsh et al. [118] were the first to observe and describe the reduction of As(V) in a background of sea water or buffer (pH 7, HEPES) on an Au microwire catalyzed by the system Mn^{2+}/Mn . We have confirmed this effect for As(V) determination in a sodium sulfite background electrolyte with the carbon composite electrode Au/CB/PE and used it for speciation analysis [86,119]. The As(V) signal was also obtained in the presence of Fe ions after electrolysis with carbon composite [104] or iron-modified carbon paste electrodes [120]. Several works on As(V) determination have been carried out with electrodes modified with reducing agents, including hematite (Fe_2O_3) [121,122] and L-cysteine [123]. It has been suggested that the hydrogen generated during the electrolysis plays the role of reducing agent for As(V) on Au and/or Pt electrodes [28,29].

There are therefore many ways to use anodic stripping voltammetry for As(V) detection with different electrodes and electrolytes, even without removal of oxygen from the solutions. This makes it possible to accelerate the whole speciation analysis and determine the total amount of As in the form As(V) without any reduction step.

4. As(III) and As(V) determination in mixture (speciation analysis)

Arsenic (III) can be selectively determined in the presence of As(V) because it is possible to choose a background electrolyte or potential at which As(V) is not reduced. However, under the conditions at which As(V) can be electrochemically reduced (see Table 1), As(III) will also be simultaneously accumulated on the electrode but with different kinetics. The signals of their anodic oxidation are at the same potential but the currents are not additive. Thus, there is a problem with the separate determination of As forms in the mixture. There are several approaches to solving this problem.

1. The separation of As forms by means of existing techniques. For example, solid-phase or liquid extraction followed by electrochemical detection of the separate forms [8,9,20]. This approach is used in the analysis of complex matrices, and is implemented in the LC + ICP-MS method [6,14,15].
2. As(V) can be determined indirectly as the difference between total arsenic concentration C_{tot} and selectively determined $C_{\text{As(III)}}$. There are two possibilities in which the C_{tot} can be defined in the form of As(III) or as As(V). The first approach is more sensitive but requires more time as it is performed in two stages. First, all As forms are oxidized up to As(V); then they are reduced to As(III). The following

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