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## Voltammetric determination of inorganic arsenic

Zhong-Gang Liu <sup>a,b</sup>, Xing-Jiu Huang <sup>a,\*</sup><sup>a</sup> Nanomaterials and Environment Detection Laboratory, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China<sup>b</sup> Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

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## ABSTRACT

Arsenic is a notorious poison and one of the world's greatest environmental hazards. Electrochemical techniques hold great promise for detecting or monitoring arsenic because they are highly sensitive, easy to perform, and low cost. We present and discuss the voltammetric determination of inorganic arsenic. In combination with an effective preconcentration (or deposition) step, voltammetry, as one of the most powerful techniques in electroanalysis, achieves the sensitive measurement of trace arsenic. On the basis of organic and biological molecules and inorganic nanomaterials, such as As(III)-specific ligands, enzymes, carbon nanotubes, graphene, and nanoparticles of noble metals (gold, silver and platinum), we comprehensively review electrochemical voltammetry for the detection of inorganic arsenic [As(III) and As(V)]. Also, we show how potential obstacles are overcome using chemically-modified electrodes. Finally, we cover future development and applications based on electrochemical techniques.

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## 1. Introduction

Arsenic (As), a notorious poison, is now recognized as one of the world's greatest environmental hazards and has threatened the lives of several hundred million people. In natural waters, As exists as arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA)

and dimethylarsinic acid (DMA), and as various organoarsenicals. Among these, the inorganic forms of As(III) and As(V) are the predominant species in natural water, and they are more toxic and have greater mobility.

There are areas in countries, such as Bangladesh, China, Vietnam, India, Chile, USA and Canada, suffering from As contamination [1,2], where As levels are above the World Health Organization (WHO) provisional guideline value of 10  $\mu\text{g L}^{-1}$  (10 ppb) for drinkable water. There are world-wide about 140 million people who drink ground-water containing unsafe levels of As. Long periods of ingesting

\* Corresponding author. Tel.: +86 551 6559 1142; Fax: +86 551 6559 2420.  
 E-mail address: [xingjiuhuang@iim.ac.cn](mailto:xingjiuhuang@iim.ac.cn) (X.-J. Huang).

groundwater with high concentrations of As is associated with chronic arsenicosis, such as “blackfoot” disease, atherosclerosis, hypertension, hyperkeratosis and different forms of skin and lung cancers [2–4].

To date, many laboratory-based analytical methods have been employed for determination of inorganic As, including atomic fluorescence spectrometry (AFS) [5], hydride-generation atomic absorption spectrometry (HG-AAS) [6], inductively-coupled plasma mass spectrometry (ICP-MS) [7], electro-spray MS (ES-MS) [8], and high-performance liquid chromatography with chemical-vapor generation (HPLC-CVG) [9]. However, these traditional laboratory-based measurements require expensive, ponderous and sophisticated instruments, high operating costs and complicated sample-preparation processes with digestion or some clean-up steps, which are time consuming and limit the application for routine field monitoring of such huge numbers of samples. Also, the changes in physicochemical properties of the samples may occur during their collection. As an alternative, electrochemical methods are acceptable as they are efficient in As determination with excellent properties (e.g., high sensitivity, ease of use, and short analysis time). Furthermore, electrochemical methods are quite different from other most analytical methods as they do not require generation of AsH<sub>3</sub>(g) hydride, which is very toxic and would otherwise have to be managed.

As a result, increasing research interest has stimulated the development of electrochemical techniques. However, there are few reviews on the voltammetric determination of inorganic As. Also, the reports are incomplete or are limited to certain environmental matrices [10–12]. Considering the great achievement of voltammetric determination of inorganic As and the continual development of electrochemical techniques, it is therefore timely to evaluate the success and to identify the challenges.

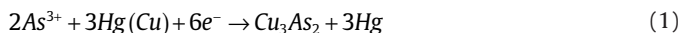
This review summarizes and discusses the development in the past seven years of the voltammetric determination of inorganic As from the points of view of methodology, design and mechanism, and potential obstacles or limitations. Tables give detailed information on As analysis. Also, we highlight the key challenges and the opportunities for further development and applications.

## 2. Principle of electrochemical detection of inorganic arsenic

As we know, several voltammetric techniques were developed and researched for determination of inorganic As, such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV) [12,13]. Among of these techniques, SWV and DPV can offer better sensitivity with higher signal-to-noise ratios, and can be used as extremely powerful tools for measuring trace levels of inorganic As. SWV, DPV and LSV are mainly based on stripping analysis to achieve the sensitive measurement of trace As, and their remarkable sensitivities are attributed to the combination of an effective preconcentration (or deposition) step, in which As is deposited onto the electrode from the solution [14,15]. The stripping analyses with SWV, DPV and LSV are generally in the forms of square wave anodic/cathodic stripping voltammetry (SWASV, SWCSV), differential pulse anodic/cathodic stripping voltammetry (DPASV, DPCSV) and linear sweep anodic/cathodic stripping voltammetry (LSASV, LSCSV).

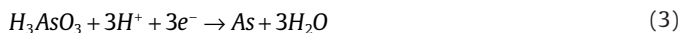
For detection of inorganic As, cathodic stripping voltammetry (CSV) is generally applied in conjunction with mercury electrodes. In the detection process, the presence of Se(IV) or Cu(II) is necessary. Taking Cu(II), for example, an intermetallic compound (Cu<sub>x</sub>As<sub>y</sub>) is probably formed on the mercury surface in the pre-electrolysis of As(III). This entire process involves the formation of a copper amalgam with As pre-concentration in highly acidic media and further scanning in the cathodic direction to obtain peak due

to the formation of arsine [10,16]. The process for As(III) determination is well described as follows:



So far, numerous works have been developed based on the CSV method and a low limit of detection (LOD) can be achieved on detection of As [16,17]. It has also demonstrated that the presence of Cu(II) [or Se(IV)] with its concentration and highly acidic media play an important role in the detection of As. However, the limitations with CSV are obvious with the oxygen reduction interfering with the CSV signal, the generation of arsine gas, and the toxicity of mercury. Fortunately, some creative works are ongoing, such as the amalgam electrode [18] and the bismuth-film electrode [19].

It is worth noting that anodic stripping voltammetry (ASV) continues to be one of the most powerful techniques for electrochemical determination of As. ASV can be performed instead of CSV to avoid production of arsine and interference from oxygen. In this case, As(III) is preconcentrated and reduced to As(0) on the surface of working electrode, in which the preconcentration is implemented by cathodic deposition at a controlled time and potential. Following the preconcentration step, the stripping step is performed in a anodic scan mode to achieve the reoxidation of As(0) to As(III) [14,20]. The oxidation current (stripping current) is recorded as a function of scan potential, which is used for detection and quantification of inorganic As. The detailed information can be obtained in Equations (3) and (4).



It should be recognized that, in the ASV procedure, overlapping stripping peaks and formation of intermetallic compounds are common, and are caused by the similarity in oxidation potentials [20–22]. Meanwhile, the unwanted adsorption of surface-active organic compounds on the working electrode would inhibit the deposition of As and affect the peak parameters of As [23]. A great deal of attention has therefore been given to this topic in order to achieve the robust, sensitive detection of As without interferences, as described in the following sections.

## 3. Electrode or substrate for inorganic arsenic analysis

With respect to the working electrode, the ideal characteristics are under careful consideration (i.e., reproducibility, selectivity, sensitivity, long-term stability, portability, ease of use, and cost effectiveness) [15]. Different types of electrode continue to be developed, such as glassy carbon electrode (GCE) [20,21,24], diamond electrode [23,25], graphite electrode [26], carbon-paste electrode (CPE) [27], screen-printed electrode (SPE) [22], Ag electrode [28], Au electrode [29–31], Pt electrode [32], and mercury electrode [16,33].

In ASV analysis, the gold electrode is the most suitable electrode for determination of As. The solid gold electrode as a substrate has been very useful for preparation of the self-assembled monolayers (SAMs) [34]. Its advantages are apparent with the high hydrogen overpotential and favorable reversibility, which result in the higher, well-defined stripping peak of As. However, the high cost, the memory effect and the formation of oxide film should not be ignored. Fortunately, various carbon-based electrodes have been explored as convenient substrates on which gold is electro-deposited or gold nanoparticles (AuNPs) are modified. These carbon-based electrodes (e.g., GCE, SPE, and CPE) possess the advantages of low background current, disposability, great simplification and flexibility in

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