



# Electrochemical generation of arsenic volatile species using a gold/mercury amalgam cathode. Determination of arsenic by atomic absorption spectrometry



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## ABSTRACT

The electrochemical generation of arsenic volatile species (arsine) using an Au/Hg amalgam cathode in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, is described. Results were compared with those obtained with other cathodes commonly used for generation of arsine. The effects of the electrolytic conditions and interferent ions have been studied. Results show that the Au/Hg cathode has better tolerance to interference and higher repeatability than cathodes made out of platinum (Pt), gold (Au), reticulated glassy carbon (RGC), lead (Pb). Under optimized conditions, a 0.027 μg L<sup>-1</sup> (3σ) detection limit for As(III) in aqueous solutions and a 2.4% relative standard deviation for a 0.1 μg L<sup>-1</sup> As(III) were obtained. The accuracy of the method was verified by determination of As in a certified reference material. The proposed method was applied to the determination of As in spiked tap water samples.

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## 1. Introduction

Inorganic arsenic compounds are generally more toxic than the corresponding organic species [1]. Arsenic intoxication symptoms are noticeable some 30–60 min after exposition [2]. Extensive and intensive exposition could be lethal. Additionally the International Agency for Cancer Research, IACR, has identified arsenic and its derivatives as possible cancer producing compounds. According to the Environmental Protection Agency maximum allowed arsenic concentration in drinking water must be below 50 μg L<sup>-1</sup>. Whereas the World Health Organization (WHO) limits it to 10 μg L<sup>-1</sup> [3,4]. In air, As concentration varies between 0.4 and 30 ng m<sup>-3</sup> [5,6], it has been estimated that 30–85% of these arsenic amounts are absorbed by the general public via respiratory inhalation [7,8]. Thus, development of a methodology for determination of As in water, air and biological samples such as blood and urine, at very low concentration levels, with sufficient accuracy and precision, is an important task.

Vapor generation (VG) coupled to atomic absorption spectrometry (AAS) could be the core of the right methodology for determination of As in different types of samples in which the element is present at very minute amounts [9–11]. Its main advantages include the possibility of separation of the analyte from its

matrix with the inherent minimization of matrix interferences and the possibility of analyte pre-concentration, leading to increased measurement capacity. This instrumental combination, VG and AAS, should allow for enough accuracy and precision of the results obtained even at the low levels of concentration in which As is encountered in some samples of interest. Chemical generation (CHG) of arsenic hydride, i.e., arsine (AsH<sub>3</sub>) generation, is the most popular way of vapor generation of this element for analytical purposes. However, this approach implies the use of solutions of reductant reagents which are contaminant, perishable and expensive. Electrochemical hydride generation (EchG) has been proposed as an alternative to the chemical way. EchG consists of reduction of the element in a cathode surface in an electrolytic cell followed by reaction of the metallic element with hydrogen generated in the cell or present in the reaction media [12]. EchG produces hydrides as efficiently and reproducibly as CHG but in a cleaner, less expensive and better controlled way. EchG has been used for arsenic determination via formation of AsH<sub>3</sub> as a means for sample introduction into atomic absorption or atomic fluorescence spectrometers, inductively coupled or microwave induced plasmas [11]. Although we were not able to find conclusive evidence on the mechanism of electrochemical formation of arsine, to date there is general agreement on the formation of this hydride according to the following steps [13–17]. Firstly, water molecules and arsenic species are electrochemically reduced to produce atomic hydrogen and metallic arsenic,

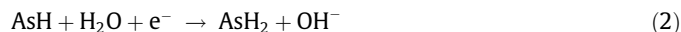
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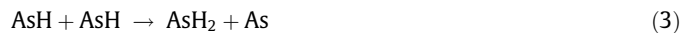
respectively. Secondly, atomic hydrogen is chemisorbed on the metallic arsenic to form a covalent hydride according to reaction (1).



Thirdly, the covalent hydride reacts with water according to



Fourthly, two hydride molecules react as follows:



Fifthly, arsine is generated by disproportionation between AsH and AsH<sub>2</sub> according to



According to the cathode material there are two general classifications; those with high hydrogen absorption power and low hydrogen over-voltage and those with low hydrogen absorption power and high hydrogen over-voltage [18]. Materials with low hydrogen over-voltage are useful because of their tolerance to interferences but at the cost of low efficiency in hydride formation. High hydrogen over-voltage cathode materials are more prone to interferences but are more efficient and more versatile in regards to hydride formation. Unfortunately, some of these cathodes present low mechanical stability and therefore must be periodically replaced [19]. The search for a convenient cathode material for ECHG with high hydrogen over-voltage, acceptable freedom from interference and sufficient mechanical stability, is still on. Electrochemical arsine generation is well documented in the literature [21–36]. The present work proposes a methodology for electrochemical arsine generation using a mechanically stable gold cathode whose hydrogen over-voltage is increased by means of mercury amalgamation. The effectiveness of the methodology has been demonstrated by determination of As in a standard reference material and in a spiked acidified tap water sample by atomic absorption spectrometry.

## 2. Experimental

### 2.1. Reagents

Working As(III) aqueous solutions were prepared by dilution of standard commercial 1.000 mg L<sup>-1</sup> As(III) solutions using distilled/deionised water, 18 MΩ resistivity, with the appropriate concentration of H<sub>2</sub>SO<sub>4</sub> (0.5 M). To evaluate the possible interference effect of Sb(III), Se(IV), Co(III), Cu(II), Fe(III), Ni(II), solutions of these metals were prepared by dilution of standard commercial 1.000 mg L<sup>-1</sup> solutions of each metal. These solutions were added to the analyte working solutions. Solutions of digested marine sediment reference material PACS-2 (National Research Council of Canada), with a certified As concentration of 26.2 ± 1.5 mg/kg and a spiked tap water sample were used for accuracy checking. Argon, 99.99% was used as purging gas. All chemical reagents were of analytical grade unless otherwise specified.

### 2.2. Instrumentation

To study the electrochemistry characteristics of the cathode materials a PAR 273-A potentiostat, was used. A power supply Extex model 382202, constant current–constant voltage power supply unit, operated in the constant current mode was used as a generator of current during the electrochemical reaction. A Shimadzu AA-6300 (P/N 206-51800) spectrometer equipped with a flame heated T-type quartz tube atomizer (14 cm length and

1.5 cm inner diameter) was used for the atomic absorption measurements. Arsenic and mercury hollow cathode lamps (Hamamatsu L2433) operated at 10 mA and at the 193.7 nm (As) and 253.7 nm (Hg) wavelength was used as a radiation source.

### 2.3. Electrochemical hydride generation

The electrochemical generation cell has been described in detail in our previous publications [20,21]. It consists of a compartment which houses a tubular chamber made out of glass (5.5 cm<sup>3</sup>) where the electrochemical reaction is held, a cathode (Au, Pt, Pb, RGC or Au/Hg) and a spiral platinum anode which completely surrounds the cathode. This particular design permits easy exchange of the cathode material, reducing the time required for replacement or cleaning. The cell possesses two glass channels, one for sample injection, and another one, perpendicular to the sample injection channel, which carries a flow of argon to transport the gaseous species produced by the electrochemical reaction, towards a gas–liquid separator and from there to the quartz atomization cell for measurements. The main goals aimed at during design of the cell were compactness, easy of assembly and improved sensitivity of the measurements with respect to pneumatic nebulisation. The use of low amounts of reagents and samples was also an important criterion considered during the design of the cell. These requirements were better fulfilled by a cell operating in the batch mode than by a cell operating in the continuous flow mode. The cell was connected to the atomic spectrometer, then a solution containing a known concentration of As, was injected to the tubular glass chamber and the gas flow rate was started at a value previously set. Application of a constant electrolytic current (galvanostatic electrolysis) generated the gaseous products of interest which were then introduced into the heated quartz atomization cell by virtue of a flow of argon, via a gas–liquid separator, to subsequently detect the arsenic content. Initial operating conditions for ECHG of As are summarized in Table 1.

For the Au/Hg amalgamation process, the Au wire electrode was cleaned with concentrated HNO<sub>3</sub> and placed in contact with pure mercury for 12 h. Times longer than 12 h were also used, but no significant effects were observed.

### 2.4. Determination of hydrogen evolution potential

An electrochemical cell with the usual three electrode arrangement consisting of the working electrode under study, a platinum coil as counter electrode and saturated calomel (ECS) reference electrode, were used to check by cyclic voltammetry the hydrogen evolution potential of the pure Au and the Au/Hg cathodes.

### 2.5. Sample preparation

Samples of interest were a marine sediment Standard Reference Material and an As spiked tap water solution. For analysis of the reference material a 0.4634 ± 0.0001 g sample was treated with 3 mL of a mixture of HNO<sub>3</sub>:HF:HClO<sub>4</sub> (3:3:1) and heated in a microwave oven during 20 min at 90% of the total power, 800 W. The

**Table 1**  
Initial operating conditions for arsine electrochemical generation.

Parameter	
Cathodic materials	RGC, Pb, Au, Pt, and Au/Hg
Cathode surface area (cm <sup>2</sup> )	3
Anode material	Pt (wire in the shape of a spiral)
Electrolytic current (A)	0.6–0.8
Supporting electrolyte (M)	H <sub>2</sub> SO <sub>4</sub> 0.5 M
Argon flow rate (mL min <sup>-1</sup> )	50

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