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# Determination of the different oxidation states of As and Sb by a new electrochemical hydride generator coupled with atomic fluorescence spectrometry

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## ABSTRACT

A novel disk electrochemical hydride generator has been developed for the determination of As and Sb. Compared with the traditional thin-layer cell, the disk cell combined the advantages of quick assembly and easy operation. This electrochemical system for hydride generation in neutral buffer solutions has been studied for analytical usefulness in coupling with atomic fluorescence spectrometry. It was found that the use of neutral phosphate buffer solution could markedly increase the fluorescence intensity of As(III) and Sb(III) and reduce the impact of cathode erosion on the stability of signal intensity. At the same time, the fluorescence intensity of As(V) and Sb(V) were almost suppressed totally. The detection limits ( $3\sigma$ ) of  $0.031 \mu\text{g L}^{-1}$  As(III) and  $0.026 \mu\text{g L}^{-1}$  Sb(III) in aqueous solutions were obtained, respectively. The precisions ( $n = 11$ ) for  $20 \mu\text{g L}^{-1}$  As(III) and Sb(III) were 2.0% and 2.7%, respectively. The method was successfully applied for determination of different oxidation states of As and Sb in environmental samples.

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## 1. Introduction

As a potentially clean approach, an electrochemical hydride generation (Ec-HG) technique has been investigated recently [1–6]. This technique is based on the reaction between hydrogen atoms derived from the cathode of an electrolytic cell and hydride forming elements [7]. Compared with chemical hydride generation (CHG) technique based on reaction between sodium (or potassium) tetrahydroborate and hydride forming elements [8–11], the Ec-HG technique alleviates the use of sodium tetrahydroborate in high-purity acidic medium as the reduction system. The  $\text{NaBH}_4$  is an expensive reagent and is susceptible to introducing contamination; its aqueous solution is unstable and it has to be freshly prepared each

working day. Moreover, the Ec-HG method uses less sample and reagent volume.

In general, the Ec-HG system includes three components: a sample injection system, an electrolytic hydride generator and a gas–liquid separator [12]. The main component of this system is the electrolytic hydride generator. Three different types of electrolytic hydride generators are described in the literature: batch generator [13], continuous flow generator [14] and flow injection generator [15]. The use of batch hydride generators is antiquated and time-consuming. Hueber and Winefordner [14] designed a flow electrolytic cell for introduction for ICP-OES. The generator consisted of a cathode flow cell immersed in electrolytic solution and held by a cylindrical container. This outer cylindrical container is referred

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below as the anode compartment and contained the anode itself. A porous glass frit covered a slot in the cathode cell wall and allowed electrical conduction between the two electrodes. However, this generator has a complex design and large inner volumes. Lin et al. [15] and Brockmann et al. [16] designed a simple electrolytic cell named thin-layer cell. This cell combined the advantages of continuous analysis with a high cathode surface to volume ratio. A flow-through version of this cell design has been reported [17] but needs daily maintenance in order to pre-treat the cathode surface. The cell is held together with screws. Due to frequent replacement or treatment of cathode, it is prone to leakage and has a short lifetime. Laborda et al. [18] and Zhang et al. [19] designed a tubular electrolytic cell with a concentric arrangement and a carbon cathode. An anode made of a coil of Pt wire surrounded the cathode tube. A PTFE tube is used as anode chamber and the cathode chamber is placed inside. Both ends are closed with PTFE pieces sealed with an epoxy resin. It leads to difficulty in changing the cathode.

Now, the determination of different oxidation states of As and Sb in real samples has become an interesting issue because of their different toxicities [20]. It should be noted that the Ec-HG does not depend on the oxidation state when using cathode materials with high hydrogen over-potential like Pb. So, it is dissatisfactory for the determination of As and Sb in different oxidation states by the Ec-HG technique. Some reports [21] detected oxidation state of As by Ec-HG with Pt cathode, however, both the detection limit and sensitivity were dissatisfactory.

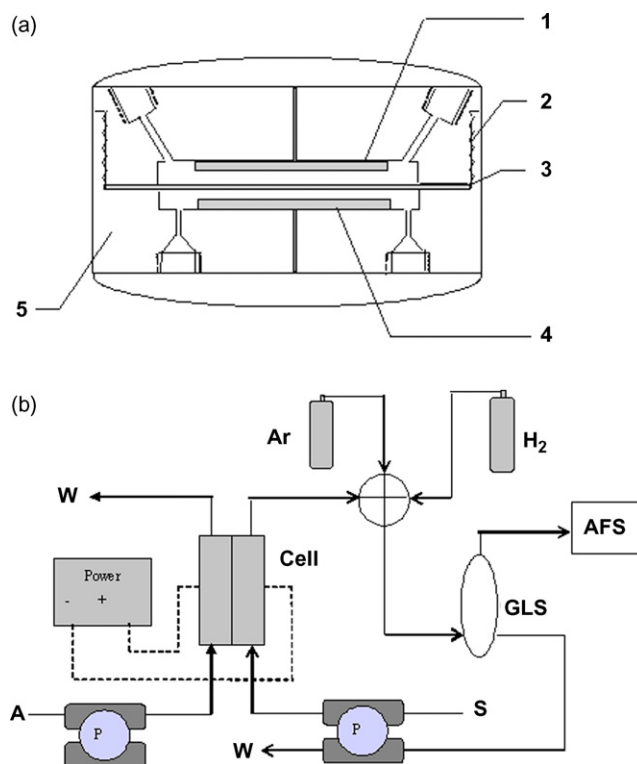
The aim of this work is to design a new electrolytic cell for the determination of different oxidation states of As and Sb. The use of neutral electrolyte was evaluated and the reasons for the signal enhancement were also discussed. The influences of several parameters on Ec-HG were investigated. The analytical figures of merit of the technique and its susceptibility to interferences were evaluated. The proposed method has been successfully applied to the determination of different oxidation states of As and Sb in water samples.

## 2. Experimental

### 2.1. Apparatus

The thin-layer disk electrolytic cell was used as hydride generator consisting of a zinc foil or Pb foil (50 mm × 10 mm × 0.2 mm) and a Pt foil as cathode and anode, respectively (Fig. 1a). Power supply for the electrolytic cell was Model 8511B constant current and constant voltage unit (Yong Heng Electrochemical Instrument Co., Yanbian, China) working in the constant current mode.

A model AFS-230 double-channel atomic fluorescence spectrometer (Beijing Haiguang Instrument Co. Ltd., Beijing, China) was employed throughout the study. Arsenic and antimony high performance hollow cathode lamps are especially designed for AFS measurement. The lamp currents were set to 60 mA and 80 mA and wavelength to 193.7 nm and 217.6 nm for arsenic and antimony, respectively. Quartz tube (7 mm i.d. × 14 mm length) was used



**Fig. 1 – Schematics of the disk electrolytic cell (a) and Ec-HG system (b). 1: cathode, 2: sealing by screw thread, 3: PTFE gasket and ion-exchange membrane, 4: anode, 5: PTFE body; A: analyte, P: pump, S: sample, W: waste, GLS: gas liquid separator, AFS: atomic fluorescence spectroscopy.**

as the atomizer. The negative high voltage of photomultiplier was 320 V. A hydrogen–argon–air entrained flame was maintained with the addition of auxiliary hydrogen. Two sequential gas–liquid separators were used for separating the gas and liquid as described in our previous work [19].

### 2.2. Reagents and samples

All reagents were of highest available purity or at least analytical grade. Doubly deionized water (DDW) was used throughout. Stock solutions (1.000 g L<sup>-1</sup>) of As(III) and As(V) were prepared by dissolving As<sub>2</sub>O<sub>3</sub> (The Chemical Reagent Company of Shanghai, Shanghai, China) and Na<sub>2</sub>HAsO<sub>4</sub>. Stock solutions (1.000 g L<sup>-1</sup>) of Sb(III) and Sb(V) were prepared from Sb<sub>2</sub>O<sub>3</sub> (The Chemical Reagent Company of Shanghai, Shanghai, China) and KH<sub>2</sub>SbO<sub>4</sub>. A series of standard solutions were prepared daily by stepwise diluting the stock solutions with 1.0 mol L<sup>-1</sup> phosphate buffer solution (PBS) or HCl just before use.

High-purity KCl, K<sub>2</sub>SO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, and K<sub>2</sub>HPO<sub>4</sub> at various concentrations were used to test the effects of the electrolytic solutions on the hydride formation efficiency. 1.0 mol L<sup>-1</sup> PBS is prepared by dissolving 13.6 g KH<sub>2</sub>PO<sub>4</sub> and 22.8 g K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O in 100 mL water. A 10% (m/v) L-cysteine solution was prepared by dissolving L-cysteine (The Chemical Reagent Company of Shanghai, Shanghai, China) in DDW.

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