Microchemical Journal 93 (2009) 180–187

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

# Electrochemical hydride generation for the determination of hydride forming elements by atomic fluorescence spectrometry

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ARTICLE INFO

*Article history:*
Received 28 May 2009
Received in revised form 3 July 2009
Accepted 3 July 2009
Available online 14 July 2009

*Keywords:*
Electrochemical hydride generation
Hydride forming elements
Traditional Chinese medicine

ABSTRACT

The determinations of As, Bi, Ge, Sb and Se were performed by atomic fluorescence spectrometry following their electrochemical hydride generation. An electrochemical hydride generator based on a screw-thread seal arrangement, working in a continuous flow mode was used. The effects of cathode material, shape and area of material, catholyte, sample flow rate, applied current, catholyte solution concentration and interference of transition metals on signal intensity were studied. Five kinds of materials including lead, graphite, copper, tungsten and platinum with different shapes were tested as cathode materials. The signal obtained from a 3-dimensional electrode was higher than that from a 2-dimensional electrode under the same conditions. The signal intensity of Ge in $HNO_3$ medium within a narrow concentration range of 0.05–0.10 mol $L^{-1}$ was stronger than that in other acidic medium, such as HCl and $H_2SO_4$. However, the signal intensity of Ge was rapidly decreased with $HNO_3$, HCl and $H_2SO_4$ concentration increasing, and then reached approximately zero. In general, limits of detection and a precision were improved using a graphite cathode in $H_3PO_4$ medium. The analysis of the reference materials showed good agreement with the certified values for As, Bi, Ge, Sb and Se. The method was successfully applied in the determination of As, Bi, Ge, Sb and Se in traditional Chinese medicine samples.

## 1. Introduction

For the treatment of diseases, traditional Chinese medicines (TCMs) are widely used in China. One of the major problems in TCMs usage is the issue of safety related to the presence of toxic metal elements with high concentrations in some products. Several severe cases associated with heavy metal, such as As, Sb, Hg, etc., have been reported [1,2]. These fatalities have severely destroyed the reputation of TCM materials. The toxicological and physiological behaviors of these elements are strongly dependent on their concentration. As and Sb accumulate easily in organisms and will cause deleterious effects on human beings when the contents exceed the allowable limit [1]. Bi is an active ingredient used in various pharmaceutical products; it can form a mucosa which is able to prevent the surface of ulcer from eroding by stomach acidity and proteinase [2,3].

Recently, the importance of Ge and Se to human health has become a focus. For example, Se deficiency can lead to heart disease and a weakened immune system which could be cured via ingesting Se-accumulating TCMs [4]. Hence, the determination of As, Sb, Bi, Ge and Se in TCM samples is very important for the safe application of TCM.

For the determination of hydride forming elements, the chemical hydride generation (CHG) techniques coupled with atomic spectrometry (AS) has been a well-established method [5–7]. The CHG-AS technology has attracted more attentions owing to its better sensitivity and selectivity. However, there are also some disadvantages. For example, the determination of Ge must be carried out in a narrow range and at a relatively low acidity. Gou et al. [8] reported the use of 3 mol $L^{-1}$ phosphoric acid allows Ge generation in the presence of high concentration of strong acid. They also developed a method for the determination of trace amounts of Ge by utilizing the vaporization of germanium tetrachloride in the high concentrations of HCl [9].

In order to solve these problems, an electrochemical hydride generation (Ec-HG) method has been developed recently [10–16]. Even the detection limit of Ec-HG technology is poor compared with CHG technology; the advantages of Ec-HG are still obvious. Firstly, it avoids the utilization of sodium tetrahydroborate ($NaBH_4$) in high-purity acidic medium as the reduction system. Secondly, the Ec-HG method uses smaller sample size and less reagent volume. Thirdly, the analysis of different oxidation state could be carried out by changing electrolytic conditions: current, catholyte and cathode material [17,18]. The early application of Ec-HG was reported based on a batch electrolytic hydride generator with NaOH as the electrolyte to the determination of arsenic by Rigin et al. [19] in 1970s. However, the use of batch hydride generators is outdated and time-consuming; the technology could not draw people's

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doi:10.1016/j.microc.2009.07.001

attention. A rebirth of Ec-HG as a sample introduction technique occurred in the early 1990s. Lin et al. [20] and Brockmann et al. [21] developed flow through electrochemical generators for continuous and flow-injection generation of hydrides. Then, Laborda et al. [22] and Zhang et al. [23] developed a tubular electrolytic cell with reticulated vitreous carbon (RVC) or graphite tube cathode, the process of hydride generation was curried out under a lower current density and a higher sample flow rate conditions. Moreover, Ec-HG has been combined with numerous analytical techniques, including atomic absorption spectrometry, atomic fluorescence spectrometry and inductively coupled plasma atomic emission spectrometry [24]. Most of the hydride forming elements was reported successfully by Ec-HG in the last fifteen years, and the technique was also applied in analysis of water, medicines and biological samples [25]. Many papers reported the determinations of As, Sb, Se, however, only a few reports on the determination Bi and Ge by Ec-HG with ICP–TOF–MS [26] or ICP–AES [27] were found. To the best of our knowledge, there is no report concerning the determination of Bi, Ge and Se in TCM samples using Ec-HG coupled with AFS.

The aim of this work is to expand the application of Ec-HG technology coupled with atomic fluorescence spectrometry. Five elements including As, Bi, Ge, Sb and Se in TCM samples were detected. The self-made disk type electrolytic cell was used for hydride generator. The effects of several parameters on Ec-HG were investigated. The analytical figures of merit of the technique and its tolerance to interferences were evaluated.

## 2. Materials and methods

### 2.1. Apparatus

A model AFS-230 double-channel non-dispersive atomic fluorescence spectrometer (Beijing Haiguang Instrument Co., Beijing, China) was employed throughout the experiment. A high-intensity arsenic, antimony, selenium, bismuth and germanium hollow cathode lamp (General Research Institute for Nonferrous Metals, Beijing, China) was used as the radiation source, which have advantages over electrodeless discharge lamps in terms of both the stability and lifetime. A quartz tube (7 mm i.d. × 14 mm length) was used as the atomizer, into which the volatile species was swept by an argon flow. A hydrogen–argon–air entrained flame was maintained with the addition of auxiliary hydrogen. Two sequential gas–liquid separators were used for getting better hydride transfer efficiency in our work, which depended on gravity to separate the gas and liquid phases. The second separator was a U-tube for further removing liquid from hydrides. The AFS instrumental conditions are summarized in Table 1.

### 2.2. Hydride generation system

A schematic of the Ec-HG–AFS system is shown in Fig. 1. Power supply for the electrolytic cell was DH1719A-3 constant current and constant voltage unit (Beijing Da Hua Wireless instrument Co, Beijing, China) working in the constant current mode. IFIS-C peristaltic pumps (Xi'an Ruimai Electronic Technology Co., Ltd., Xi'an, China) was used to transport the samples.

**Table 1**
Operating conditions of the Ec-HG–AFS system.

| Parameter | As | Bi | Ge | Sb | Se |
|---|---|---|---|---|---|
| HCL current (mA) | 60 | 80 | 80 | 80 | 80 |
| Negative high voltage of photomultiplier (V) | | | 320 | | |
| Quartz furnace height (mm) | | | 8 | | |
| Wavelength (nm) | 193.7 | 306.8 | 265.2 | 217.6 | 196.0 |
| Ar flow rate (mL min$^{-1}$) | | | 600 | | |
| Electrochemical hydride generation | | | | | |
| Hydrogen flow rate (mL min$^{-1}$) | | | 320 | | |
| Anolyte (mol L$^{-1}$) | | | 0.5 $H_2SO_4$ | | |
| Catholyte (mol L$^{-1}$) | | | 1.0 $H_3PO_4$ | | |
| Sample flow rate (mL min$^{-1}$) | | | 0.5 | | |
| Cathode | | | Graphite sheet (5 cm$^2$) | | |
| Electrolytic current (A) | | | 2.0 | | |

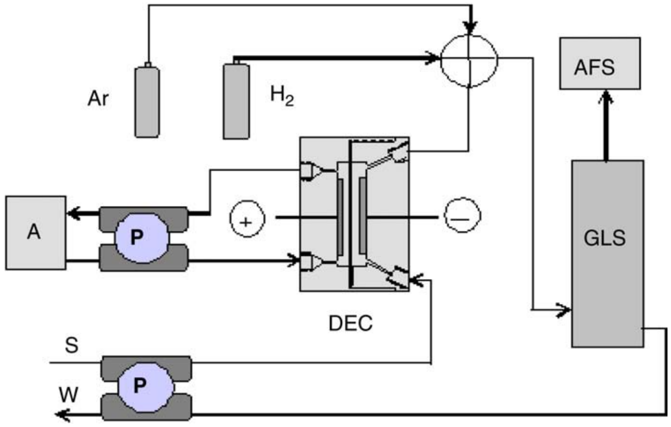

**Fig. 1.** Schematics of the Ec-HG system. A anolyte solution, P pump, DEC disk electrolytic cell, S sample, W waste, GLS gas–liquid separator, and AFS atomic fluorescence spectroscopy.

Two types electrolytic flow through cells (denoted I and II) were used to evaluate the quality of electrode. Cell I, described previously [18], consisted of a disk electrolytic flow through cell. The Polytetrafluoroethylene (PTFE) body of the cell consists of a cathodic and an anodic (both 55 × 11 × 2 mm, inner volumes of 1.2 mL). The cathode and the anode are embedded in them, separated by two slotted PTFE gaskets with an ion-exchange membrane (Huanyu Company of Beijing, Beijing, China) in between. The two compartments are held together with screw-thread for easy dismounting of the cell. A Pt foil anode was fixed on channel bottom of the anode cell. Cell II which consisted of a graphite tube with drilled holes as the cathode and a platinum wire anode (0.25 mm diameter, 100 mm length) was described previously [12]. A polytetrafluoroethylene (PTFE) cylinder (28 mm i.d., 45 mm length) and a screw-cap with a holed cylinder (8 mm i.d., 1.5 mm thickness, 32 mm length) covering the graphite tube construct the cell chambers. The cathode body is wrapped up in a cation ion-exchange membrane to isolate the electrogenerated gases. Some materials such as Pb foil, graphite, Cu foil, W wire and Pt foil were used as cathode and the surface area was about 5 cm$^2$.

### 2.3. Chemical reagents

All reagents were of highest available purity, and of at least analytical grade. Doubly deionized water (DDW) was used throughout the experiment. Stock solutions (1.000 g L$^{-1}$) of As (III) and As (V) were prepared by dissolving $As_2O_3$ (The Chemical Regent Company of Shanghai, Shanghai, China) and $Na_2HAsO_4$. Stock solutions (1.000 g L$^{-1}$) of Sb (III) and Sb (V) were prepared from $Sb_2O_3$ (The Chemical Regent Company of Shanghai, Shanghai, China) and $KH_2SbO_4$; 1.000 g L$^{-1}$ stock solution of Se (IV) and Se (VI) were prepared by dissolving appropriate amount of selenious acid and $Na_2SeO_4$ (The Chemical Regent Company of Shanghai, Shanghai, China); 1.000 g L$^{-1}$ stock solution of Ge and Bi were prepared by commercial standard solutions (National standard material center of China). A series of standard solutions were prepared daily by stepwise diluting the stock solutions just before use. The Tea leaf reference material GBW 08505 and the River sediment reference material GBW 07318 (Research Center for Eco-Environmental Sciences, the Chinese Academy of Sciences, China) were applied to evaluate the accuracy of the proposed method. High-purity HCl, $H_2SO_4$, $HNO_3$ and $H_3PO_4$ were used to test the effects of the electrolytic solutions.