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Selective determination of four arsenic species in rice and water samples by modified graphite electrode-based electrolytic hydride generation coupled with atomic fluorescence spectrometry

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ABSTRACT

This work describes a novel non-chromatographic approach for the accurate and selective determining As species by modified graphite electrode-based electrolytic hydride generation (EHG) for sample introduction coupled with atomic fluorescence spectrometry (AFS) detection. Two kinds of sulfydryl-containing modifiers, L-cysteine (Cys) and glutathione (GSH), are used to modify cathode. The EHG performance of As has been changed greatly at the modified cathode, which has never been reported. Arsenite [As(III)] on the GSH modified graphite electrode (GSH/GE)-based EHG can be selectively and quantitatively converted to AsH_3 at applied current of 0.4 A. As(III) and arsenate [As(V)] on the Cys modified graphite electrode (Cys/GE) EHG can be selectively and efficiently converted to arsine at applied current of 0.6 A, whereas monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) do not form any or only less volatile hydrides under this condition. By changing the analytical conditions, we also have achieved the analysis of total As (*t*As) and DMA. Under the optimal condition, the detection limits (3 s) of As(III), *i*As and *t*As in aqueous solutions are 0.25 μg L^{-1}, 0.22 μg L^{-1} and 0.10 μg L^{-1}, respectively. The accuracy of the method is verified through the analysis of standard reference materials (SRM 1568a).

1. Introduction

It is well-known that arsenic is one of the most hazardous elements to human health. Arsenic exists in soil, atmosphere, and natural waters [1]. Besides, transformation processes within environment can result in different arsenic forms, which are available for plant uptake, and also can enter the food supply. The extensive research demonstrates that rice and rice products could be one of the main sources of arsenic because rice plants are especially efficient at accumulating arsenic from their anaerobic environment [2]. Due to different toxicities of different chemical forms of arsenic, there is a great demand for an accurate rapid analysis technique to monitor various arsenic species, especially for highly toxic inorganic arsenic in water and rice samples [1–3].

Chemical hydride generation (CHG) coupled with atomic or ionic specific detectors, such as atomic absorption (AAS), atomic fluorescence (AFS) or inductively coupled plasma-mass spectrometry (ICP-MS), is a powerful technique for arsenic determination because of simplicity and efficiency [4]. Generally, speciation of As is performed by two different analytical approaches: (i) hyphenated separation techniques (*e.g.* chromatographic-based method [5]) and (ii) selective generation of the different hydride. As we known, As(III) and As(V) can be reduced to arsine (AsH_3) by sodium or potassium salts of tetrahydroborat(III). MMA and DMA can be reduced to CH_3AsH_2 and $(CH_3)_2AsH$ respectively by the same reagent [6]. Actually, the differences in the boiling points of these arsines documents that they can be separated by freeze all of arsines and volatilization with gradual warming. For example, Musil et al. utilized cryogenic trap to preconcentrate and separate arsine and methylsubstituted arsines coupled AFS detection, which is an extremely sensitive method to the determination of the toxicologically As species in water samples and in human cells [7]. Some researches show that the generation efficiency of these arsines can be controlled by the careful choice of reaction conditions in terms of pH, type of acid or buffer, borohydride concentration, or additives [8–11]. Thereafter, As(III), As(V), MMA and DMA can be selectively determined without the use of any separation techniques. For instance, Matoušek et al. reported a hydride generation-cryotrapping-ICP-MS (HG-CT-ICP-MS) method for arsenic speciation analysis at picogram levels [8]. Shraim et al. developed a method for determination of four As forms by controlling acidy and reducing agent concentration with or without Cys assistance [11]. Pitzalis et al. established a selective CHG

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method of DMA in the presence of As(III) and MMA in their excelled works by using borane-ammonia (AB) as a reducing acid in the presence of Cys and in 0.5 M $HClO_4$ [12]. Another study documents that the concentrations of As(III) and As(V) in the sample can be calculated according to the equations of response obtained at two selected conditions owing to the different ratio of slopes of the calibration curves for As(III) and As(V) under optimized conditions [13]. In comparison with chromatographic methods, selective CHG methods are still attractive because they can offer simple, fast, and inexpensive ways to speciation analysis. However, some problems of CHG, such as expensive reducing agents, poor stability and low tolerances of transition metals, puzzled researchers [14]. For ultra-trace analysis, the purity of $NaBH_4$ may also become a limitation for controlling the CHG blank level [15].

Since Golloch et al. [16] and Huang et al. [17] firstly introduced flow injection electrolytic cell in 1990s, the interest for the application of electrolytic hydride generation (EHG) as sample introduction in atomic spectrometry has been growing. Only inorganic electrolyte solutions (acidic, basis or salt) are required in EHG to ensure electric current for reduction process [18]. Hence, EHG technique not only eliminates the reagent problem of conventional CHG, also provides simple reactions and a green analytical method [19]. In the last twenty years, many papers have been published based on EHG for analyzing As [18,20–22], Bi [22,23], Cd [24,25], Ge [22,26], Hg [27,28], Pb [29], Sb [21,22,30], Se [18,31], Sn [32], Tl [33], Te [34] and Zn [35] in tobacco, food, water, medicine and soil, *etc.* Meanwhile, the EHG behaviors of As(III) and As(V) can be distinguished by adjusting the electrolysis conditions (*e.g.* changing cathode material [22] or using suitable electrolytes [36,37]), which indicates that EHG is a possible way for species analysis of inorganic arsenic instead of chromatographic (or other) separation [38]. The similar results were also found in Sb [20] and Se [18] determination.

In comparison to inorganic ions, there are only a few papers that focused on the electrochemical reduction of organic element compounds. Ding and Sturgeon [18] firstly investigated the EHG behaviors of four species As on Pb cathode. EHG efficiencies of arsenic from As(V), MMA, DMA and arsenobetaine (AB) obtained in their study were $92 \pm 7\%$, $86 \pm 6\%$, $56 \pm 10\%$, and none, compared to that from aqueous As(III). Obviously, analyzing inorganic arsenic (*i*As) in the complex samples could be seriously interfered by organic arsenics (*o*As). Shen and Dasgupta [39] found that As (III) responded about 4-fold greater than As(V) on highly oriented pyrolytic graphite (HOPG) cathode. On Al cathode, the responses of As(III) and As(V) are similar. 100 μg L^{-1} MMA on HOPG produced a signal equivalent to ~40% of 10 μg L^{-1} As(V). DMA was even less sensitive. Then Shen and Dasgupta established a method for exclusive measurement of *i*As in their excellent works. Tu et al. [40] reported a hyphenated technique for species analysis of four forms of As by ionic chromatography (IC) and EHG-AFS. Except for As(III), the data of other arsenic forms were unclear in their experiment.

Numerous documents have confirmed that thiolic compounds (*e.g.* Cys) in combination with different acids, under certain pH conditions, can dramatically change the reaction efficiency of different arsenic species in the CHG techniques [11,12,41,42]. We also found that Cys modified graphite electrode can achieve the conversion of CH_3Hg^+ to Hg vapor [43]. For these reason, we have studied the different EHG behaviors among four As species on the –SH modified electrodes in this paper, and on those results that also present interesting implications in selective arsenic species determination, with exact, inexpensive and sensitive. To the best of our knowledge, this work is the first study of application of EHG for the determination of four arsenic forms in real samples without chromatographic technique.

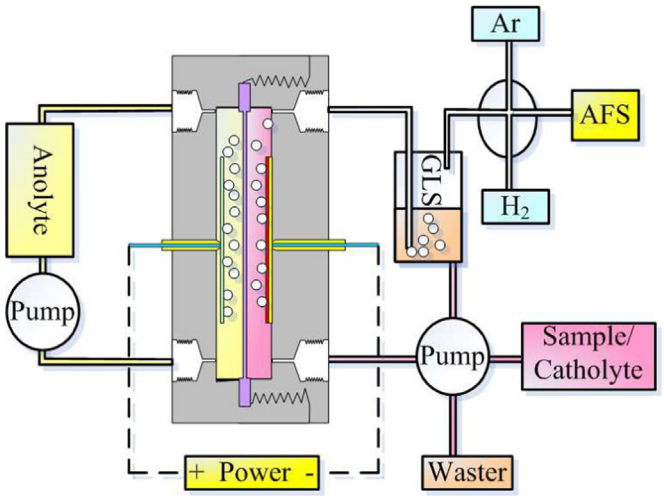

Fig. 1. Schematics design of manifold and instrumental setup used for EHG-AFS determination of As. GLS gas liquid separator; AFS atomic fluorescence spectrometry.

2. Experimental

2.1. Standards, reagents, and components

Analytical grade reagents are used throughout whenever available. Details of reagents and other components and sources are given in Supplementary material.

2.2. Apparatus

As shown in Fig. 1, the EHG-AFS system consisted of three modules: the sample injection module composed of two 4-channel peristaltic pumps (IFIS-C, Xi'an Mairui Electronic Science and Technology Co., Xi'an, China). The hydride generation module including a homemade disk shaped thin-layer electrolysis cell and a constant current and constant voltage unit (DH1719A-3, Beijing Dahua Wireless instrument Co, Beijing, China). Power supply for the electrolytic cell is working in the constant current mode. The detail of disk cell is similar with our pervious work [43]. The detector module consisting of a nondispersive atomic fluorescence spectrometry (AFS-230, Beijing Haiguang Instrument Company, China) and a coded hollow cathode lamp (HCL) of arsenic (193.7 nm), which is operated in a double-modulated pulsed mode to offer stable and high intensity radiation. Two sequential gas-liquid separators (GLS) are used to separate the gases from liquid. The atomizer is a quartz furnace in a shielding mode, which is composed of a concentric inner tube (7 mm i.d × 14 mm length) and outer shielding tube (10 mm i.d × 18 mm length). Around the top of quartz furnace outlet is a resistance wire to ignite the gas mixture of argon, hydrogen and volatile analysts produced from the EHG module. The flame is maintained with addition of auxiliary hydrogen.

2.3. Modified electrode preparation

Two sulfhydryl modified electrodes, a glutathione modified graphite electrode (GSH/GE) and a L-cysteine modified graphite electrode (Cys/GE), were prepared respectively. Before modification, the bare graphite electrode (commercially available from local market) is polished to the size of about 50 mm × 10 mm × 1 mm by abrasive paper and fine alumina slurries on a polishing cloth. Then the electrode is rinsed with water, sonicated for 10 min, rinsed with methanol, and allowed to dry. Modifiers are immobilized on GE by two steps: (i) GE is