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# Low temperature hydrogen plasma assisted chemical vapor generation for Atomic Fluorescence Spectrometry



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## ARTICLE INFO

### Article history:

Received 16 December 2013

Received in revised form

7 March 2014

Accepted 10 March 2014

Available online 27 March 2014

### Keywords:

Low temperature plasma

Chemical vapor generation

Atomic Fluorescence Spectrometry

Arsenic speciation

## ABSTRACT

Chemical vapor generation techniques have long been considered as important ways of sample introduction for analytical atomic spectrometry. In this paper, a low temperature plasma assisted chemical vapor generation method which avoids the massive use of consumptive chemical agents was proposed by using atmospheric pressure dielectric barrier discharge. The plasma was generated by hydrogen doped argon gas flow through a quartz tube, serving as a dielectric barrier, which had a copper wire inner electrode and a copper foil outer electrode. An alternative high voltage was applied to electrodes to ignite and sustain the plasma. Sample solutions were converted to aerosol by a nebulizer and then mixed with the plasma to generate hydrides. To confirm the utility of this method, four hydride forming elements, As, Te, Sb and Se, were determined by coupling the low temperature plasma assisted chemical vapor generation system with an atomic fluorescence spectrometer. Responses of As, Te, Sb and Se were linear in the range of 0.5–20  $\mu\text{g mL}^{-1}$ . The RSDs of As, Te, Sb and Se in the present method were less than 4.1% and the absolute detection limits for As, Te, Sb and Se were 0.6 ng, 1.0 ng, 1.4 ng and 1.2 ng, respectively. Furthermore, four arsenic species were determined after HPLC separation. The method is green and simple compared with hydride generation with tetrahydroborate and the most attractive characteristic is micro-sampling. In principle, the method offers potential advantages of miniaturization, less consumption and ease of automation.

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## 1. Introduction

Chemical vapor generation coupling to atomic spectrometry has been widely applied to determine trace elements in environmental and biological samples [1,2]. This technique has gained popularity owing to its superiority in terms of sensitivity, selectivity and linear range for the determination of hydride-forming elements, such as As, Te, Sb and Se from trace to ultra-trace levels [3]. Hydride generation by sodium tetrahydroborate ( $\text{NaBH}_4$ ) has been applied successfully in separating analytes from the matrix to reduce interference and in pre-concentrating the analytes [4,5]. However, tetrahydroborate is so unstable and difficult to store that it should be used immediately after preparation [5]. In addition, those chemical agents are quite consumptive during the analysis; therefore the method of hydride generation by tetrahydroborate does not conform to the principle of energy conservation and emission reduction.

To avoid shortcomings of the conventional hydride generation method, various reducing agents and sources of nascent hydrogen have been suggested in order to convert the elements into hydrides,

although the mechanism for the formation of hydrides is still a matter of debate [6–9]. Sturgeon's group has reported an approach of vapor generation; in the presence of low molecular weight organic acid solutions, inorganic Se(IV) is converted by UV light to volatile Se species, which are rapidly transported to a heated quartz tube atomizer for detection by atomic absorption spectrometry [10]. Wang et al. have explored a method for online pre-reduction of Se(VI) with a newly designed UV/ $\text{TiO}_2$  photocatalysis reduction device [11], which could be applied to selenium speciation by coupling HPLC to the atomic fluorescence spectrometer [12]. Zhang et al. have developed a method of electrochemical HG system which consists of a graphite tube cathode and a platinum anode for analyses of As, Sb [13] and Hg [14]. Techniques mentioned above have partly overcome the disadvantages of conventional hydride generation, but inorganic or organic reagents are still required, which possibly pollute the environment.

These problems can be solved by generating nascent hydrogen in hydrogen plasma by dielectric barrier discharge (DBD) without chemical agent, provided that the production of nascent hydrogen in DBD plasma has been previously demonstrated [15]. As a mature means to create low temperature plasma (LTP), DBD which has been successfully used in previous studies of atomic spectrometry, offers several advantages like forming at atmospheric pressure, small size and low power consumption [16,17]. A DBD source with argon or helium plasma has been reported as an atomization source, or to

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provide energy for atomic emission processes. For instance, a wall-stabilized argon plasma for the determination of some volatile hydride-forming elements has been reported [18]. Gras et al. and Hou et al. have explored the DBD as a gas chromatographic (GC) detector [19,20]. A DBD atomizer for AAS or AFS has been proposed by our group for the determination of hydride-forming elements [21,22,24,26,27] and further extended to serve as the light source of atomic emission spectrometry by Wang's group [23,25]. Also the combination of LTP with ICP-MS proved that LTP probe is easily coupled to various elemental analysis tools for thin layer or direct solid sample analysis in microarea [28]. Recently, Zhu et al. have reported a plasma-chemical vapor generation of cadmium [29]. However, analyses of common hydride generated elements, such as As, Te, Sb and Se, have not been successful. Since a large number of active hydrogen species, such as H, H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, and H<sub>3</sub><sup>+</sup> exist in H<sub>2</sub> plasma [30], and these species possess much higher reduction abilities than molecular H<sub>2</sub>, we proposed to use a hydrogen plasma to replace the hydrides generation system with NaBH<sub>4</sub> for the elemental analysis.

In the present work, we used hydrogen plasma to generate chemical vapors without the use of NaBH<sub>4</sub>, organic acid and other chemicals such as TiO<sub>2</sub>. Four elements have been examined including As, Te, Sb and Se by coupling the low temperature plasma assisted hydrides generation method with the atomic fluorescence spectrometer. The proposed method was validated by analyses of certified reference materials (kelp, laver and underwater sediments). Also, a mixture of four arsenic species has been analyzed after HPLC separation. The results met with our expectation that the chemical vapor generation can be generated in a DBD-hydrogen plasma.

## 2. Experimental section

### 2.1. Reagents

All chemicals were at least of analytical grade and all solutions were prepared using ultra-pure water with a resistivity of 18.2 MΩ cm, obtained from a water purification system (Thermo Fisher, USA). The stock standard solutions of Se, Te, As and Sb (1000 mg L<sup>-1</sup>) were supplied by National Analysis Center for Iron and Steel (Beijing, China). Working standard solutions were prepared daily by stepwise dilution of stock solutions with 5.0% (v/v) hydrochloric acid. Argon (99.999%) and hydrogen (99.999%) from Huayuan Co. (Beijing, China) were used and the flow rates were controlled and measured by two mass and volumetric flow controllers (Cole-Parmer Co. Ltd., USA).

For conventional HG-AFS, 2.0% (m/v) NaBH<sub>4</sub> solution was prepared by dissolving the appropriate amount of NaBH<sub>4</sub> into 0.5% (m/v) NaOH. For arsenic speciations, arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) standard solutions were provided by National Institute of Metrology (NIM). The HPLC eluent was prepared with (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Merck), and the pH was adjusted to 6.0 by addition of an aqueous NH<sub>3</sub> solution (Merck).

### 2.2. Instrumentation

A commercial AFS was employed in the present study (AFS 9800, Hai Guang Co., China). High-intensity hollow cathode lamps (General Research Institute for Non-ferrous Metals, Beijing, China) were used as light sources. The optimized experimental conditions of AFS used for this study are summarized in Table 1. High voltages from a DBD pulse generator (Coronalab Co. Ltd., Nanjing, China) were applied to the central copper wire and the outer electrode. The HPLC system consisted of a six-port valve with a 100 μL injection loop (Rheodyne), a Hamilton PRP X-100 anion-exchange

**Table 1**  
The operation conditions of AFS.

Parameters	As	Te	Sb	Se
Lamp primary current (mA)	60	60	70	80
Lamp boost current (mA)	30	30	35	40
Negative high voltage of PMT (V)	300	300	290	300
Shield gas flow rate (mL min <sup>-1</sup> )	900	900	900	900
Atomizer observation height (mm)	8	8	8	8

column (250 mm × 4.1 mm i.d., 10 μm) and a guard column packed with the same material. The outlet of the column was connected to on-line continuous DBD-hydrogen plasma – Atomic Fluorescence Spectrometry system.

### 2.3. Samples

To validate the accuracy of the developed method, the certified reference materials, underwater sediments (GBW07311), kelp (GBW08517) and laver (GSB-14) were obtained from the National Research Center for Certified Reference Material of China. Samples were decomposed by a microwave-assisted digestion system. Briefly, 0.5 g of the samples was added to Teflon vessels containing 6.0 mL HNO<sub>3</sub> and 2.0 mL HCl for GBW07311, 4.0 mL HNO<sub>3</sub> and 2.0 mL H<sub>2</sub>O<sub>2</sub> for GBW08517 and GSB-14, respectively. Teflon vessels were closed tightly and put into the microwave digestion system (MARSS, CEM, USA) for digestion. The heating program was 120 °C for 5 min, 140 °C for 5 min, 160 °C for 15 min and 185 °C for 5 min. After cooled to ambient temperature, digests were quantitatively transferred into a Teflon volumetric flask. The residues were flushed with ultra-pure water into the volumetric flask and the solutions were adjusted to the finally contained 5% (v/v) HCl.

For arsenic speciation analysis, 0.2 g of the pulverized sample was added into the extraction cell at room temperature and 10.3 MPa pressure with 50% (v/v) methanol solution. Then it was extracted for 5 min and purged by nitrogen for 60 s. This procedure was repeated three times; the combined extracts were extracted with rapid swirling flow concentrator and concentrated at 65 °C. After the concentrate was diluted with ultrapure water and fixed weighed to 25.0 g, the sample solution was obtained.

### 2.4. Safety consideration

In case of the high voltage shock, contacting the electrode should be avoided during generating the plasma. Direct glaring at the plasma should also be avoided to prevent harm from ultraviolet radiation.

## 3. Results and discussion

### 3.1. Design of the LTP assisted chemical vapor generation system

The schematic diagram and pictures of experimental setup used in the present study are shown in Fig. 1. The copper wire and copper foil served as electrodes, while the quartz served as the dielectric barrier. The copper wire was sealed inside a quartz tube to avoid the contamination of samples and was placed at the center of a quartz cell. When a high voltage was applied to electrodes, the plasma was ignited and sustained. The plasma could easily be generated in Ar or a mixture of Ar with He, N<sub>2</sub> or H<sub>2</sub> at atmospheric pressure.

The experiments were carried out by coupling DBD-hydrogen plasma with AFS for the determination of As, Sb, Te, and Se samples at the concentration of 10 μg mL<sup>-1</sup>. The standard solutions were introduced into the system by a syringe at a flow rate of 10 μL min<sup>-1</sup>, respectively. After nebulization with argon gas,

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