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Technical note

A simple electrochemical hydride generation apparatus for the determination of inorganic arsenic in food samples with an atomic fluorescence spectrometer

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ABSTRACT

A simple electrochemical hydride generation (EcHG) apparatus was developed for arsenic determination by atomic fluorescence spectrometry. The apparatus consists of two graphite tubes (as the atomizer in graphite furnace atomic-absorption spectrometry) that were used as cathode and anode cells and are connected together in series by an insulated plastic pipe, an AC to DC power wall plug adapter (12 V 2 A) used with portable computers, and a gas-liquid separator. The apparatus did not include an ion-exchange membrane, and an analyte solution containing thiourea and hydrochloric acid was used for both electrolytes without a specific anode only solution. The experimental results showed that EcHG efficiencies and detection limits depended on the output voltage and the concentration of HCl and thiourea used. Under the optimized conditions (solution flow rate of 3 ml mim^{-1}, carrier argon gas flow rate of 400 ml min^{-1}, a 12 V 2 A DC power adapter, and concentrations of thiourea and HCl of 1%(m/v) and 10%(*v*/v), respectively), the limit of detection of arsenic was 0.3 ng ml^{-1} (3σ), and the relative standard deviation was 4% for ten consecutive measurements of a 40 ng ml^{-1} As(III) standard solution. The calibration curve was linear up to 100 ng ml^{-1}. The accuracy of the method was verified by the determination of arsenic in two certified reference materials (GBW10045 for rice flour and GBW10015 for spinach), and the results were in good agreement with the certified values.

1. Introduction

Chemical vapor generation (CVG) based on sodium tetrahydroborate (THB) is a popular technique for trace analysis due to several advantages such as the separation of the analyte from the matrix, high analyte introduction efficiency and excellent sensitivity (detection limit) [1–3]. However, this technique also has several disadvantages such as high reagent cost and the instability of THB in solutions. In addition, some transition and noble metals had been found to interfere with CVG based on THB. For these reasons, it is highly important to develop new VG techniques that can replace the traditional CVG based on THB. Currently, such alternative methods include photochemical vapor generation (Photo-CVG) [4–7], electrochemical vapor generation (EcHG) [8,9], and pyrolysis chemical vapor generation (Py-CVG) [10].

As an alternative to CVG based on THB, EcHG had been widely studied and developed for the past few decades, and a number of papers related to this topic have been published for analyzing various elements introduced as samples by atomic spectrometry [8,9,11–17]. However, the current EcHG apparatus is usually quite complicated and must be carefully designed and fabricated and therefore is unsuitable for the fast assembly and application in real sample analysis. In a current EcHG apparatus, first, an ion exchange membrane or glass frit is required to separate the two electrolysis cells and two electrolytes must be pumped into the two electrode chambers, respectively. Second, the corrosion of metal electrodes made of metals such as lead, cadmium and Pb—Sn alloy may cause environmental pollution and interfere in the determination. Although the use of an apparatus without a membrane has been reported [14,16], these are still somewhat complicated due to the need for a constant voltage unit and the use of different materials for the fabrication of the EcHG apparatus.

In this study, a simple, low-cost, easily assembled EcHG apparatus that does not include either an ion-exchange membrane or a constant voltage unit was developed for the determination of inorganic arsenic in the food samples by non-dispersive atomic fluorescence (AFS).

2. Experimental

2.1. Instrumentation

A model PF6 non-dispersive atomic fluorescence spectrometer (AFS, Beijing Puxi General Instrument Co., Beijing, China) was used in this work. A As hollow cathode lamp for AFS was used at a lamp current of 60 mA. Three repeated integration times of 17 s each were used for measuring the fluorescence intensity of arsenic. A model SPH-500 hydrogen generator (Beijing BCHP Analytical Technology Institute,

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Beijing, People's Republic of China) at a flow rate of 350 ml min^{-1} was used to form the H_2—Ar flame of the AFS atomizer. The other operating conditions for AFS were exactly the same as those described in a previous report [10].

2.2. Apparatus for EcHG

The core of this system consists of two graphite tubes and an AC 220 V to DC 12 V 2 A regulated power supply adapter.

Two new pyrolytic graphite-coated graphite tubes (28.4 mm length; 8 mm od; 6 mm id; 1 mm wall thickness, Beijing Beifen-Ruili Analytical Instruments Co., Ltd., China) that are used as an atomizer in the graphite furnace atomic-absorption spectrometry (GFAAS) were connected together in series via an insulated polyethylene plastic pipe. The distance between the two graphite tubes (i.e., the gap between the cathode and the anode) was 8 mm. After the injection ports of both tubes were sealed by rubber bars, two copper wires (positive and negative) from two output ports of the power supply adapter were tightly wound around the middle of the two graphite tubes, respectively, and then wrapped and fixed by insulating tape. The upper graphite tube that is used as the cathodic compartment was connected to the negative pole of the DC power adapter, and the lower graphite tube that was used as the anodic compartment was connected to the positive pole of the power adapter. The apparatus did not include an ion-exchange membrane and did not require a special constant-current power supply. EcHG was carried out in the continuous mode using a peristaltic pump and a gas-liquid separator [18]. The whole setup was vertically fixed so that the graphite tubes (electrolysis cells) can be filled with a feed solution (electrolyte). A schematic diagram of the EcHG apparatus is shown in Fig. 1.

2.3. Reagents and standard solutions

Working standard solutions of As(III) were prepared by the dilution of the stock standard solutions of a 1000 μg ml^{-1} As(III) stock standard solution (National Standard Material Center of China). Sulfuric and hydrochloric acids of high purity were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Thiourea of analytical purity was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Deionized water was used in all experiments.

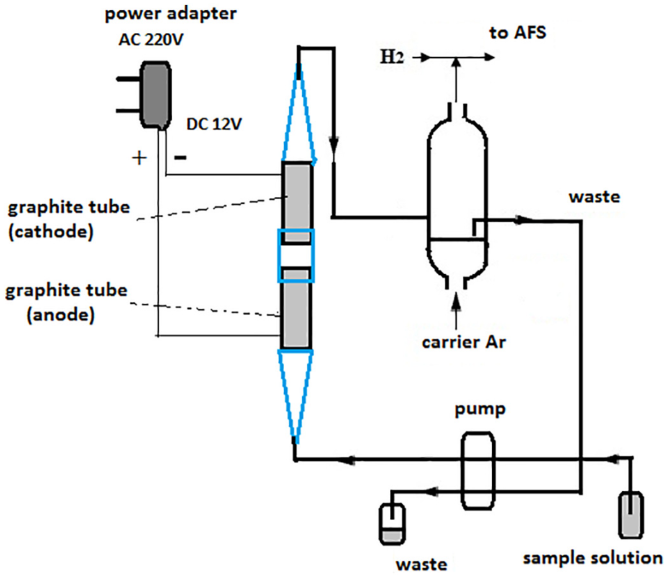

Fig. 1. Diagram of the EcHG apparatus coupled to AFS.
Two new graphite tubes were pyrolytic graphite coated tubes without platforms used as the atomizer in GFAAS and were connected via an insulated plastic pipe. The other two ends of the two graphite tubes were connected to the entrance tube and the exit tube of the solution, respectively, by two 5 ml plastic pipette tips. The central holes of every graphite tube were sealed by rubber bars to prevent solution leaks.

2.4. Sample preparation

A 0.3 g spinach (GBW10015) or a 0.6 g rice (GBW10045) was digested according to ref. [18]. After complete volatilization of $HClO4$, the residue was dissolved in 10 ml 10% HCl (*v*/v), transferred into a 25 ml volumetric flask. Then, 0.4 g solid thiourea was added to this volumetric flask and diluted to volume with 10% HCl (*v*/v).

3. Results and discussion

3.1. Apparatus

3.1.1. Graphite tube

Clearly, an EcHG apparatus with tubular electrodes connected in series without an ion-exchange membrane is the easiest to assemble and implement in a short time. In this work, four kinds of hollow tube electrodes were examined on the basis of the design shown in Fig. 1. The experiments were performed under the following conditions: arsenic concentration was 40 ng ml^{-1}; the concentrations of thiourea and HCl were 1% (m/v) and 10% (*v*/v), respectively; the solution flow rate was 3 ml min^{-1}, and the carrier argon gas flow rate was 400 ml min^{-1}. First, it was found that two graphite tubes currently in use, denoted as No.1 in Table S1 (Appendix A), can produce a very good signal intensity of 1200 (a.u.); second, when two small graphite tubes (24.2 mm length, 6.9 mm o.d., 5 mm i.d., 0.95 mm wall thickness; pyrolytic graphite coated tube used as the atomizer in GFAAS) as No.2 in Table S1 (Appendix A) were tested, a net fluorescence intensity of 450 (a.u.) can be observed; third, when two other small graphite tubes (35.1 mm length, 6.1 mm o.d., 3.9 mm i.d., 1.1 mm wall thickness, used as an industrial electrode), denoted as No.3 in Table S1 (Appendix), were tested, a lower net fluorescence intensity of 250 (a.u.) was observed; finally, when two small titanium tubes (purity > 99%, 36.5 mm length, 4.1 mm o.d., 2.3 mm i.d., 0.9 mm wall thickness, for industrial use) as No.4 Table S1 (Appendix) were tested, the maximum net fluorescence intensity (a.u.) was only 30 (a.u.). Taking into account the difference in the parameters of the three types of the graphite tubes, we calculated the density, inner surface area and internal volume of the different graphite tubes. The parameters of the different graphite tubes are shown in Table S1 (Appendix). Although the above results showed that only graphite tubes used in GFAAS can produce very good signal intensities, especially for No.1 graphite tubes, i.e., the largest one in use in this work, those only provide a rough assessment of the performance of EcHG in different tubular electrodes. When the differences in the inner diameter or length of the graphite tubes, the residence time of the sample in the tubes and the time for the reaction will also be different. Thus, the systematic experiments should be carried out for an accurate comparison. In addition, the surface characteristics of the graphite, pyrolytic or not, will also be of significance. Clearly, the most important factor affecting EcHG and its efficiency needs to be further studied so that a better analytical performance will be obtained and the graphite tube most suitable for EcHG can be fabricated.

3.1.2. Position of the two electrodes

It is obvious that the vertical placement of the two graphite electrodes in series was optimal for obtaining the uniform contact of the solution with the inner wall of the tube. Therefore, we examined the effect of the distance between the two electrodes on the signal intensity for arsenic. It can be observed from Fig. S1 (Appendix) that the arsenic signal intensity increases with the decrease in the distance between the two electrodes. When the distance between the two electrodes was 0.6 cm, it was found that many gas bubbles were present between the two electrodes, showing that the electrolysis reaction was very intense.