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Development of a new electrochemical hydride generator with tungsten wire cathode for the determination of As and Sb by atomic fluorescence spectrometry

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Abstract

A novel electrochemical hydride generator has been developed for the determination of As and Sb. This newly devised hydride generator is constructed from a flowing electrolytic cell, in which the tungsten wire is selected as cathode. Compared with some cathode material usually used in electrochemical hydride generator, the tungsten cathode is of better interference tolerance, corrosion-resistant and longer working time. The characteristics of the cathode material, hydride generating efficiency and interferences of concomitant have been studied in detail. The detection limits (3σ) of As and Sb in sample solution were $0.10\,\mu g\,L^{-1}$ and $0.15\,\mu g\,L^{-1}$, the precisions for 11 replicate measurements of $20\,\mu g\,L^{-1}$ As and Sb were 1.3% and 1.7%. The electrochemical hydride generator coupled with atomic fluorescence spectrometry has been applied to the determination of total As and Sb in tobacco samples.

Keywords: Electrochemical hydride generation; Tungsten; Atomic fluorescence spectrometry; Arsenic; Antimony; Tobacco samples

1. Introduction

Electrochemical hydride generation (Ec-HG) has been a possible alternative method of chemical hydride generation (CHG) to analyze some hydride-forming elements recently [1–11]. Though the Ec-HG method's detection limit is inferior to that of CHG now, it could be free of some disadvantages associated with the $NaBH_4$-acid system. Moreover, the Ec-HG technique needs less sample and reagent volume. The earlier work of Ec-HG was the determination of As and Se using Pt as the anode and cathode [2–4]. Then, Lin et al. [12] and Ding et al. [13,14] designed a simple thin-layer electrolytic flow cell using carbon or Pb as cathode. The carbon or Pb cathode has higher hydrogen over-voltage and can reduce much more hydride-forming elements into hydrides. As a result, the hydride generating efficiencies of As (III) and As (V) were improved and reached 86 and 73%, respectively. Also, the Sb (III) and Sb (V) were equally converted into their hydrides with a 92 ± 4% hydride generating efficiency. Then Laborda et al. [15] fabricated a tubular electrolytic flow cell using a cathode packed with reticulated vitreous carbon (RVC) for the determination of As, Se and Sb. Their hydride generating efficiencies were all more than 90% attributing to larger cathode surface area.

Interference of concomitant, however, is a prevalent problem in both the CHG [16,17] and the Ec-HG technology [18]. Some studies [19,20] have identified copper and nickel as the most serious interferences in the Ec-HG technique. Lin et al. [11] studied the interferences of some ions and the results indicated that the interference effect strongly related to cathode material. He suggested using an appropriate cathode to minimize interferences of some elements, e.g. the interference of Cu could be negligible using Pt cathode. Brockmann et al. [3] studied the interferences of Ni and Co for the determination of Se. And similar results that influences of transition metals could be eliminated by using Pt cathode were obtained. When using Pt as cathode, as much

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as 10,000 μg mL^{-1} Ni and Co didn't appear obvious interference for the determination of As and Se. However, because of lower reduction capability, the Pt cathode can only be applied to the hydride generating of As (III), Sb (III) and Se (IV) and their hydride generating efficiencies were also less than 50%.

As for the Pb or carbon cathodes, the interferences of transition metal ions are very significant. Ding et al. [18] found, when using lead, pyrolytic graphite or vitreous carbon as a cathode, the direct interference or memory effect by transition metal ions was very severe. For example, when using Pb cathode, 120 μg mL^{-1} Cu in samples solution resulted in 30% recovery and 20 μg mL^{-1} Ni did lower 20% recovery for As (III) determination. Bolea et al. [19] researched the interference from Cu for determination of Se by using different cathode materials. In presence of Se/Cu ratios 1:100, it was observed that almost total signal was suppressed for RVC cathode and 50% signal suppression for Pb cathode. Our recent works [20] has shown that 10 μg mL^{-1} of Cu in samples solution could result in recovery as low as 53 and 22% for 50 ng mL^{-1} As (III) and Sb (III) determination, when using the common graphite tube cathode.

The main purpose of this paper was to design a sensitive and simple Ec-HG cell for the determination of trace level of As and Sb. In this work, a novel electrochemical hydride generator by using tungsten as cathode are fabricated and evaluated. The hydride generator coupling to AFS are applied to the determination of As (III) and Sb (III). The researches will focus on the characteristics of cathode material, efficiency of hydride generation and interferences of concomitant. The proposed method has been successfully applied to the determination of As (III) and Sb (III) in tobacco samples.

2. Experiments

2.1. Apparatus

A homemade thin-layer electrochemical cell was used as hydride generator for producing hydrides. 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. WX-3000 microwave oven (Shanghai EU Chemical Instruments Co. Ltd, China) was used as sample digestion.

A model AFS-230 double-channel non-dispersive atomic fluorescence spectrometer (Beijing Haiguang Instrument Co., Beijing, China) was employed throughout. Arsenic and antimony high performance hollow cathode lamps (General Research Institute for Nonferrous Metals, Beijing, China) are especially designed for AFS measurement, which have advantages over electrode-less discharge lamps in both the stability and lifetime. Quartz tube (7 mm i.d. × 14 mm length) was used as the atomizer. The argon flow and hydrogen flow were controlled by rotameter, respectively. Two sequential gas–liquid separator (GLS) was used to isolate the gas from liquid.

2.2. Regents

All reagents were of highest available purity, and of at least analytical grade. Doubly deionized water (DDW) was used throughout. Stock solutions (1.000 g L^{-1}) of As (III) and As (V) were prepared by dissolving As_2O_3 and $Na_2HAsO_4{\cdot}7H_2O$ (Beijing Chemicals Co. Ltd., Beijing, China). Stock solutions (1.000 g L^{-1}) of Sb (III) and Sb (V) were prepared from Sb_2O_3 and KH_2SbO_4 (Beijing Chemicals Co. Ltd., Beijing, China). A series of standard solutions were prepared daily by stepwise diluting the stock solutions with 0.5 mol L^{-1} HCl just before use.

Guarantee reagent HCl, H_2SO_4, HNO_3 and $HClO_4$ at various concentrations were used to test the effects of the electrolytic solutions. A 10% (m/v) ascorbic acid solution was prepared by dissolving ascorbic acid (The Chemical Regent Co., Shanghai) in DDW. A tea reference material (GBW07605) and a Mussel reference material (GBW08571) were purchased (Research Center for Eco-Environmental Sciences, the Chinese Academy of Sciences, China) to evaluate the accuracy of the present method. Argon of 99.99% purity was used as the carrier gas. Tungsten wire (0.2 mm diameter.), copper foil, lead foil and Pt foil (0.25 mm thick, 99.9%) are used.

2.3. Hydride generator

The proposed electrolytic cell was schematically shown in Fig. 1. It has been described similarly in publication [12]. The polytetrafluoroethylene (PTFE) cell consisted of the upper and lower chamber (both 100 mm × 10 mm × 3 mm, inner volume of 3 ml). Cation ion exchange membrane (Huanyu Co. Beijing) was used to separate the gases generated in anode and cathode chamber. A Pt foil anode is fixed on channel bottom of the anode cell. Tungsten wire was used as cathode. The tungsten wire after polishing is knitted into a multilayer and net-shaped cathode in order to increase electrode surface. The wire length is about 5 m and the surface area is about 31.4 cm^2. In addition, we also found the bubbles formed in net-shaped electrode cell were very small that could improve the flowing stability of solution.

2.4. Sample preparation

Tobacco sample were dried at 60 °C for 48 h prior to further preparation and then ground and stored in a desiccator. 0.5000 ± 0.0001 g tobacco samples and reference material samples were placed in PTFE vessels, respectively. After adding 4 ml conc. HNO_3 and 1 ml 30% H_2O_2, the vessels were sealed and placed in the microwave digestion oven for microwave-assistant digestion. The digestion program consisted of two stages: stage 1 (120 °C, 0.5 MPa, 5 min); stage 2 (140 °C, 1 MPa, 10 min). After digested and cooled to room

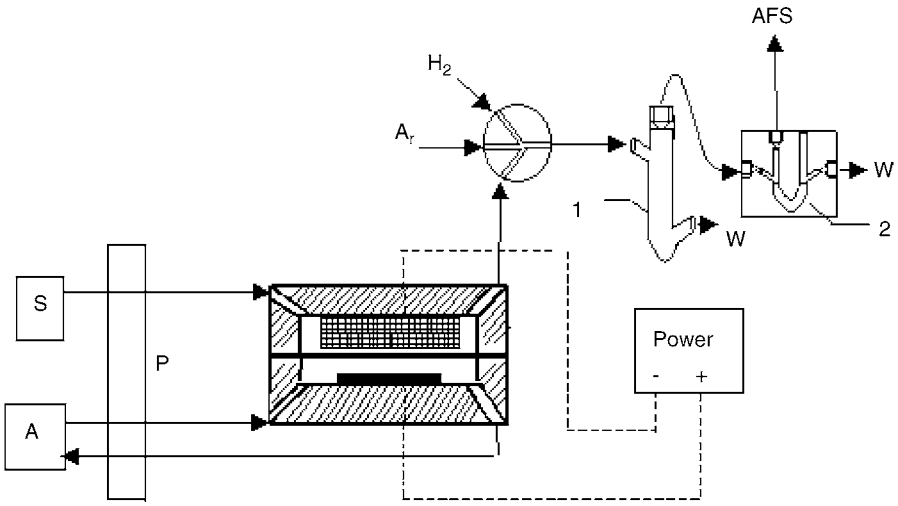

Fig. 1. the Schematics of the cell and the Ec-HG system. 1, first separator; 2, second separator; A, analyte; P, peristaltic pump; W, waste; S, sample; AFS, atomic fluorescence spectrometry.

temperature, the solution was transferred to a 50 ml beaker and heated at 120 °C to near dryness (ca. 0.5 ml). Then, the solution was transferred into a 25 ml calibrated flask, added 2.5 ml 10% ascorbic acid and diluted to volume with 0.5 mol L^{-1} HCl.

2.5. *Analytic procedures*

Electrochemical hydride generation was accomplished in continuous mode. The anolyte and catholyte solution are continuously pumped into the anode and cathode chambers of the cell at a flow rate of 2.0 ml min^{-1}, respectively. After the anode and cathode chambers are filled, the flow rate is reduced to 0.5 ml min^{-1} and starts to electrolyze at constant current mode. A voltage (ca. 6–7 V) was applied to keep the current at 1.4 A. The arsine and stibine, hydrogen and liquid waste in the cathode chamber are delivered to a cross-tube and mixed with Ar and auxiliary H_2. The gases are separated from the solution by the gas–liquid separators and directed to the detector through a PTFE tube (0.8 mm i.d., 100 mm length). Oxygen produced in the anode chamber is driven out along with anolyte. The anolyte is reclaimed and recycled. The operating conditions of the system are listed in Table 1.

Table 1
Ec-HG-AFS Operating conditions for the simultaneous determination of As and Sb

Parameter	As	Sb
Hollow cathode lamp (mA)	60	80
Negative high voltage (V)	320	320
Quartz furnace height (mm)	8	8
Wavelength (nm)	193.7	217.6
Sample flow rate (ml min^{-1})	0.5	0.5
Electrolysis current (A)	1.4	1.4
Ar flow rate (ml min^{-1})	520	520
H_2 flow rate (ml min^{-1})	300	300

3. Results and discussion

3.1. *Selection of cathode material*

An ideal cathode material should have higher hydrides generating efficiency, larger surface and good suppressing interference capability. Pt is usually used as anode for configuration of an electrolytic cell for its stability and inertia. If platinum is used as cathode, the interference of transition ions is insignificant, but it can only be applied to analyzing lower oxidation state of As, Sb and Se. The materials of higher hydrogen overvoltage, such as Pb, Cd, Hg-Ag and carbon, can bring higher hydride generating efficiency under the same conditions. However, the interference from transition ions is an unavoidable problem.

In present research, some materials that have middle-overvoltage, including tungsten and copper, are considered. Tungsten is known as a corrosion-resistant material that can be operated in acidic electrolyte. The hydrogen overvoltage of tungsten is higher than that of Pt, of course, lower than that of Pb under the same conditions. From our experimental results, we found that the tungsten cathode has better suppressing interference ability and higher hydride generating efficiency for As and Sb determination.

3.2. *Comparisons of cathode materials*

Some cathode materials were compared over the hydride generating efficiency of As (III) and Sb (III). Fig. 2 illustrates the effects of sample flow rate and cathode materials on hydride generating efficiency of As (III) and Sb (III). This results were obtained under electrolytic current 1.4 A for W cathode and 2 A for other cathodes according to their optimum conditions. It was observed that the magnitude of hydride generating efficiency were Pb > W > Cu > Pt. when using W cathode, the hydride generation efficiencies of As (III) and Sb (III) were 89.4 and 87% under the optimum con-

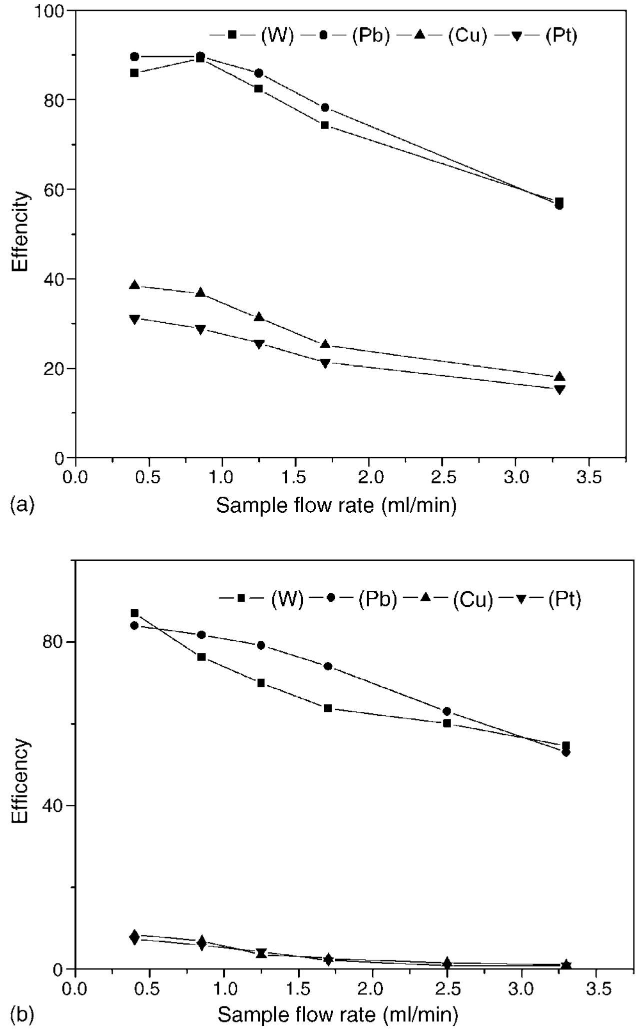

Fig. 2. (a) the effect of the cathode materials and sample flow rate on the efficiency of As. (b) The effect of the cathode materials and sample flow rate on the efficiency of Sb.

ditions, which is approximate to that of the Pb cathode. On the other hand, we also found that, under the Pt and Cu cathode, the efficiencies of As (III) were 34.5%, 38.7%, and Sb (III) were 8.4% and 7.3%, respectively.

The hydride generating efficiency of As (V) and Sb (V) is less than those of As (III) and Sb (III). Among these cathode explored in present work, the hydride generating efficiencies of As (V) and Sb (V) under Pt and Cu cathode were very low. The efficiency of As (V) and Sb (V) under W cathode was 68% and 54%, respectively, which are somewhat less than Pb cathode's 87 and 73%. As a result, As (V) and Sb (V) should be reduced prior to sample determination. This will be discussed in section 3.4 in detail. In this paper, the efficiency of hydride generating, E_{hg}, was calculated as our recent works [20].

The interferences of some ions are an inevitable problem in Ec-HG. In present work, we studied the effects of some metal ions under Pb or W cathode. The results are expressed as the recovery according to the fluorescence intensity of samples with and without interfering ions. The results indicated that the interference of transition ions, especially Cu and Co, were serious when using Pb cathode. The recoveries of As and Sb were only 74 and 67%, respectively, when the concentration of Co was 4 mg L^{-1}. The recovery of Sb was only 20% under 10 mg L^{-1} Cu. In contrast, the W electrode has better interference tolerance. In the above-mentioned conditions, the recoveries of As and Sb were all better than 90%.

Ding et al. suggested that the interference occurred on the surface of cathode when Pb was used as cathode [16]. The transition ions were reduced to elemental metal and then deposited on the surface, which will change cathode hydrogen overvoltage. Because those transition elements had lower overvoltage than that of Pb, it will result in the hydride generating efficiency of analyte decreasing. As to W cathode, because it has similar overvoltage to Cu and Ni, the deposited elements don't affect the reducing capability of W cathode. This may be why the interference of transition ions on the W cathode is insignificant.

The effects of hydride-forming elements on the determination of 50 μg L^{-1} As (III) and Sb (III) were also studied. The most of them did not effect the determination of As by proposing method. The recoveries were range from 90 to 110%. We also found that, When the Ge concentration was 1 mg L^{-1}, the recovery of determination Sb was about 87%. But in real samples, the Ge concentration is usually lower than that. As a result, As and Sb in samples can be directly determined with calibration curve.

Pb is often as cathode in Ec-HG, because it has higher overvoltage. However, the stability of Pb cathode in acidic electrolyte is not satisfying. After it is operated for a day, the fluorescence intensities of As and Sb decrease by about 50%. So Pb cathode needs pre-treatment prior to operation every working day. As to tungsten wire electrode, the experiment's results indicated that the fluorescence intensity of As and Sb didn't change obviously during a week.

3.3. Electrolytic operating conditions

Effects of HCl, H_2SO_4 and $HClO_4$ concentration in catholyte on the fluorescence intensity of 20 μg L^{-1} As and Sb were examined and the results of As is shown in Fig. 3, in which anolyte is 0.5 mol L^{-1} H_2SO_4. We can find that their effects are similar and the optimum concentration range is 0.3–1.0 mol L^{-1}. The effect of electrolytes on Sb is similar to As. Considering the stability of fluorescence intensity, 0.5 mol L^{-1} H_2SO_4 was chosen as catholyte in following work.

We also researched the effect of HNO_3 concentration in the catholyte. The result showed that the fluorescence intensities of As and Sb rapidly decreased when HNO_3 concentration was more than 0.2 mol L^{-1}. The results implied that high concentration HNO_3 maybe affect the reduction of the analyte due to itself reduction on cathode surface.

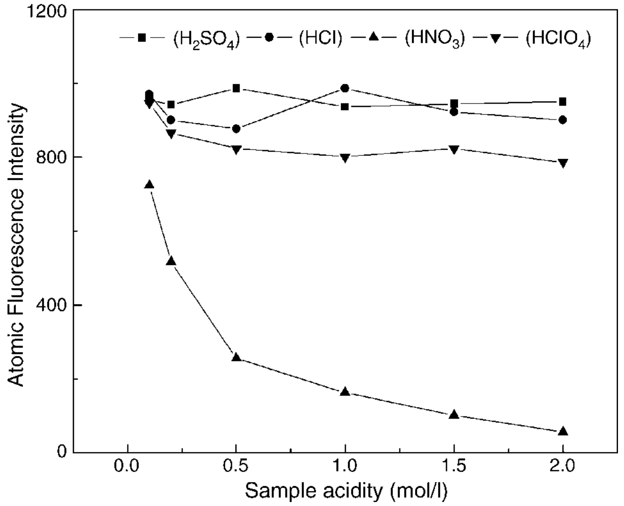

Fig. 3. the effects of the sample acidity on the fluorescence intensity of 20 μg L^{-1}As.

The fluorescence intensities increased in proportion to the electrolytic current for 20 μg L^{-1} As and Sb. They quickly increased as current increasing up to 1.2 A, and then the intensity increased slightly. After 1.8 A, the intensities levelled off. Because larger current would dramatically shorten the lifetime of the cell, in this work, 1.4 A was used and the current density was 44.6 mA cm^{-2}. Because of larger surface area of net-shaped cathode, the current density was lower, which can reduce the effect of overheating on the stability.

The hydride generating efficiency is strongly affected by the sample flow rate as shown in Fig. 2. While the fluorescence intensities of As (III) and Sb (III) increased along with sample flow rate varying from 0.3 up to 3.5 ml min^{-1}, the hydride generating efficiencies of As (III) and Sb (III) decreased to 54 and 53%, respectively. As a consequence, 0.5 ml min^{-1} sample flow rate was chosen in our work.

3.4. Auxiliary conditions

The atomization process of arsine and stibine was accomplished by the hydrogen-argon-air entrained flame. This flame could not be maintained without adding auxiliary hydrogen due to insufficient hydrogen produced from electrolysis. From experimental results, 300 ml min^{-1} H$_2$ flow rate was chosen in this work.

The mixed reducing agent (ascorbic acid + thiourea) is usually used for the pre-reducing of the analyte. Here, the reduction was carried out by ascorbic acid, and the thiourea was used for eliminating some ion interferences. However, from our experiments, we didn't find that the thiourea could eliminate interferences and this result is similar to other paper [21]. So, in following work, only the ascorbic acid was employed as the reducing agent. When the ascorbic acid was more than 1.0%, the fluorescence intensities of 20 μg L^{-1}As (V) and Sb (V) reached the same magnitude of As (III) and Sb (III), respectively. As a result, 1.2% ascorbic acid was used as the optimum reducing regent in our work.

3.5. Analytical figures of merit

Regression lines between fluorescence intensities and their concentrations are described by equations: $I_F = -27.42 + 47.39C_{\mathrm{As}}$, $I_F = -24.57 + 53.32C_{\mathrm{Sb}}$, where, C is the As or Sb concentration (μg l^{-1}). And the regression coefficients R are 0.9998 and 0.9989, respectively. Detection limits based on three times the standard deviation of the sample blank (3σ) were 0.10 μg l^{-1} for As and 0.15 μg l^{-1} for Sb. Under the optimum condition, the precisions of determination (R.S.D., $n = 6$) were 1.3 and 1.7%, respectively.

Table 2
Results of analysis of the standard reference material (mg g^{-1})

Sample	Certified value		Found value [a]		Found value [b]	
	As	Sb	As	Sb	As	Sb
Mussel (GBW 08571)	6.1 ± 1.1	6	5.75 ± 0.75	5.50 ± 0.69	5.65 ± 0.64	5.10 ± 0.81
Tea (GBW 07605)	0.28 ± 0.03	0.056 ± 0.005	0.26 ± 0.05	0.048 ± 0.009	0.30 ± 0.10	0.050 ± 0.010

[a] Determination by CHG with AFS.

[b] Determination by Ec-HG with AFS.

Table 3
Analytical results of As and Sb in tobacco samples

Samples	Found value (μg g^{-1*})		Added value (μg g^{-1})		Reclaimed (μg g^{-1})		Recovery (%)	
	As	Sb	As	Sb	As	Sb	As	Sb
1	12.3 ± 1.6	2.8 ± 0.2	20.0	2.0	33.5 ± 2.0	4.7 ± 1.2	106 ± 5	95 ± 4
2	16.8 ± 2.0	1.5 ± 0.2	20.0	2.0	35.7 ± 1.8	3.6 ± 0.8	95 ± 5	105 ± 4
3	28.3 ± 2.3	3.9 ± 0.5	20.0	2.0	51.3 ± 2.2	6.1 ± 0.6	115 ± 7	110 ± 5

[*] Determination after 20-fold dilution and mean value ± S.D. ($n = 3$).

3.6. Analytical results of standard reference material and samples

Analytical Results of As and Sb in reference material Tea (GBW07605) and Mussel (GBW 08571) listed in Table 2 are in agreement with certified values. The proposed method was successfully applied to the analysis of tobacco samples, and the results are listed in Table 3 and their recoveries are satisfying.

In this section, recovery was calculated as $R = $(reclaimed value − found value)/added value.

4. Conclusion

A novel electrochemical hydride generator with tungsten wire cathode has been developed for the determination of As (III) and Sb (III) by AFS in tobacco sample. Tungsten is known as a corrosion-resistant material that can be operated in acidic electrolyte. From present study, the tungsten wire cathode is able to restrain the interference from the transition ions. Furthermore, the hydride generating efficiency of As (III) and Sb (III) are also satisfying. In addition, employing net-shaped cathode in present system decreased the current density and prolonged the working time of cathode. The Ec-HG technology with tungsten wire cathode provides a possible analyzing method for As and Sb in biological samples.

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