

Simultaneous Determination of Trace Arsenic and Antimony in Fomes Officinalis Ames with Hydride Generation Atomic Fluorescence Spectrometry

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Abstract A robust, accurate and sensitive analytical procedure was developed for the simultaneous determination of trace arsenic and antimony in fomes officinalis ames by hydride generation atomic fluorescence spectrometry. The parameters were studied systematically, such as acid concentration of the reaction medium, flow rate of the carrier gas and shield gas, the atomizer of height, etc. Ascorbic acid, potassium iodide and thiourea were used as reducer or masking agents to enhance the generation efficiency of the volatile species of As and Sb. In the presence of thiourea, potassium iodide and ascorbic acid, the influences of some coexisting elements on the determination of arsenic and antimony were investigated.

Keywords Hydride generation atomic fluorescence spectrometry · Fomes officinalis ames · Arsenic · Antimony

Introduction

The determination of the heavy metal and the nocuous element is obligatory item which the Chinese traditional medicine has the entrance of international market. It is our country established the question which the Chinese traditional medicine quality standard still has not solved. In order to understand baseline level of the heavy metal and the harmful element in the Chinese traditional medicine, it establishes the high sensitive examination method to examine the low-content the heavy metal and the harmful element [1].

The determination of trace and ultratrace toxic elements with arsenic and antimony in trace samples has been received increasing attention concerning their environmental pollution because many kinds of pesticide and herbicide were used widely. It is very meaningful to obtain concentrations of As and Sb simultaneously. It is known arsenic and antimony can exist in two different oxidation states: As(III), Sb(III) and As(V), Sb(V). As(V) and Sb(V) react slowly with KBH_4 in HCl medium and fluorescence signals are around 50% of those provided by As(III) and Sb(III). Therefore, pre-reduction of samples is necessary for the determination of total As and Sb content [2].

In the present work, a more highly sensitive method was developed for the simultaneous determination of trace As and Sb by atomic fluorescence spectrometry (AFS) using an intermittent flow hydride generation technique [3–6]. Thiourea, as well as potassium iodide and ascorbic acid, which improved the kinetic reaction constant of hydride generation was used to enhance the hydride generation efficiency of As and Sb. It was proposed that the metal borides played a key role in catalyzing the reaction of hydride generation. In addition, this work utilized an intermittent flow hydride generation system which had some unique advantages, including minimum sample and reagent consumption, less cross contamination, less liquid-phase interference and the ability to use exactly defined sample. The method established in this paper provides high sensitivity, accuracy and precision. AAS, on the other hand, although it has been extensively used, suffers from the fact that it is non-linear and measurements at lower levels are extremely difficult. Whilst ICP-MS offers similar limits of detection to HG-AFS, it also suffers from some polyatomic interference and systems are considerably more expensive to purchase and run [7]. HG-AFS has been successfully applied to the simultaneous determination of trace arsenic and antimony in fomes officinalis ames.

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Table 1 Recommended operating conditions

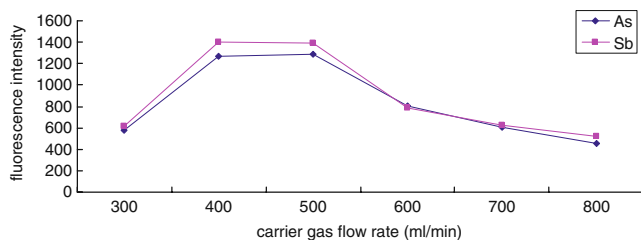
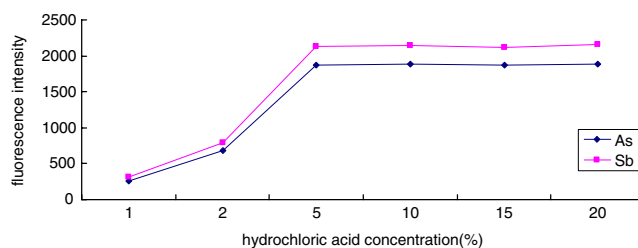
Parameter	As	Sb
Lamp current (mA)	60	80
Resonance wavelength (nm)	193.7	217.6
PMT voltage (V)	300	
Atomizer temperature (°C)	200	
Atomizer height (mm)	8	
Carrier gas flow (ml min ⁻¹)	400	
Shield gas flow (ml min ⁻¹)	900	
Read time (s)	10	
Delay time (s)	1	
Read mode	Peak area	
Measurement method	Std. curve	

In this work, As and Sb of fomes officinalis ames were determined by HG-AFS. The relevant parameters, the measurement conditions were also studied in detail.

Experimental

Reagents and Chemicals

All reagents were analytical grade and made in Beijing and Tianjin chemical factory. Double deionized water (DDW, 18.2Ω) obtained from a WaterPro water system was used throughout. Stock standard solutions of antimony (1 mg/l) and arsenic (1 mg/l) were obtained from Center of Standard Material of China (Beijing, China). A mixed working standard solution (As 100 ng/ml, Sb 100 ng/ml) was prepared daily by deionized water dilutions of the stock solutions. 2.0% m/v KBH₄ solution was prepared daily by appropriate amounts of powdered dissolving KBH₄ (Tianjin Institute of Reagents, Tianjin, China) in 0.5% m/v KOH (Beijing Chemicals Co., Beijing, China). 5% v/v HCl was prepared from 36% v/v HCl (Beijing Chemicals Co., Beijing, China). A mixed reductive solution was composed of 5% m/v thiourea, 5% m/v ascorbic acid

**Fig. 1** Effect of carrier gas on the signal of As and Sb**Fig. 3** Effect of hydrochloric acid concentration on the signal of As and Sb.

and 5% m/v potassium iodide. High purity argon (99.99%) was used to transport gas and shield gas.

Apparatus

A fully-automatic double-channel hydride generation atomic fluorescence spectrometer, AFS-230E (Beijing Haiguang Instrumentals Co. Ltd., Beijing, China), was used and controlled through a computer. An intermittent flow hydride generation system was employed throughout this work.

Methods

1.000±0.0001 g of sample was accurately weighed and evaporated to the dryness in an oven at 80°C for 2 h. Dried samples placed in a digester with 1 ml of perchloric acid and 5 ml of nitric acid. Digestions were made under conventional pressure. The resultant solutions were transferred into a 50 ml volumetric flask and finally diluted to volume with deionized water. The solutions for the determination were prepared by mixing 5 ml sample solutions with 1.25 ml of a 36% hydrochloric acid solution, 5 mL reductive solution were volume 50 ml.

Hydride generation was carried out by mixing the solutions for determination with 2.0% m/v KBH₄ solution using an intermittent flow system. The operating conditions of the instrument are presented in Table 1.

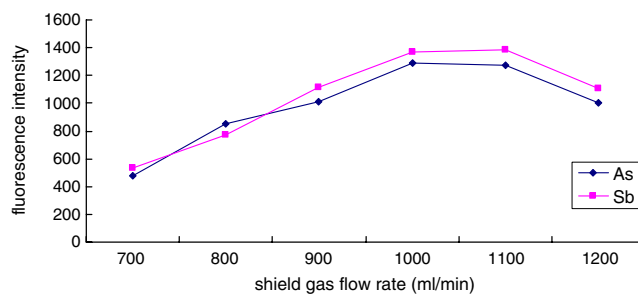
**Fig. 2** Effect of shield gas on the signal of As and Sb

Table 2 Calibration data for each analyze studied

Analyte	As	Sb
Concentration range ($\mu\text{g l}^{-1}$)	0–100	0–100
Equation of fit	$y = -0.023 + 0.276x$	$y = -0.881 + 0.351x$
Linear correlation co-efficient(<i>r</i>)	0.	0.9999

Results and Discussion

Pre-reduction Conditions

As and Sb can exist in two different oxidation states: trivalent and pentavalent. It is well known that As(V) and Sb(V) have much slower reaction kinetics for hydride formation. This is dependent on the hydride generation system used and the concentration of reagents. With a continuous flow manifold the hydride generation efficiency is around 40% compared to the trivalent oxidation state. The most common pre-reduction involves the addition of potassium iodide, thiourea and ascorbic acid reagent.

Previous results indicate that a mixture of KI and ascorbic acid provides an effective reduction to the trivalent oxidation states after a pre-reduction time of 30 min. The use of thiourea also can enhance an effective reduction. In addition, thiourea and ascorbic acid as masking reagents could reduce the interference of coexisting elements.

Carrier Gas and Shield Gas

Pure argon (99.99%) was used as both the carrier gas and the shield gas. Argon transports volatile hydrides from the liquid–gas separator to the atomizer, it acts as analyte diluent and stabilizes the flame by forming an appropriate mixture with H₂. Various flow rates, which influenced the sensitivity and stability of the instrument, were tested in this study. The effect of carrier and shield gas on the signal of As and Sb indicated in Figs. 1 and 2. The carrier gas at lower flow rate could not quickly sweep the hydride of the analyte into the inner tube of a quartz furnace, and at higher flow rate would dilute the analyte introduced in the furnace tube. Presumably, the amounts of vapor generated were different for different analytes. Different flow rates of extraneous gas were required for completely carrying the

different amounts of hydride analytes into atomizer, which led to a difference in the flow rates giving the highest signal intensity for As and Sb. The shield gas was used to prevent extraneous air from entering the flame. A flow rate of 800–1100 ml min⁻¹ for As and 800–900 ml min⁻¹ for Sb gave the highest signal intensity. A compromised carrier gas of 400 ml min⁻¹ and a shield gas of 900 ml min⁻¹ were employed for the simultaneous determination of As and Sb.

Reacting Acidity and KBH₄ Concentration for Hydride Generation

The influence of the HCl concentration in the reaction medium was investigated using 2%(m/v) KBH₄ as a reducer. The optimum HCl concentration that provided the highest relative signal for As and Sb was in the range from 5% (v/v) to 20% (v/v) (Fig. 3). It is necessary to point out that the optimum HCl concentration became higher with an increase in the KBH₄ concentration. KBH₄ was used as both a reducer and hydrogen supplier, which was necessary to keep the argon–hydrogen flame. A lower KBH₄ concentration could give higher signal intensity for Sb. But the signal intensity could be improved by using a higher KBH₄ concentration, at the same time the flame noise also increased. In this work, a KBH₄ concentration of 2% (m/v), which provided a good signal-to-noise ratio, was employed for the simultaneous measurement of As and Sb.

Investigation of Interference

If the determination procedure established is to have any practical utility, it is essential that it can tolerate the

Table 3 Results for C.R.M GBW07605 (*n*=6)

Element	As	Sb
Certified value ($\mu\text{g g}^{-1}$)	0.28±0.04	0.056±0.006
Value obtained ($\mu\text{g g}^{-1}$) ^{a,b}	0.27±0.035	0.057±0.0047
% Recovery	97.9	101.3

^a All results corrected for moisture content (i.e. 10.3%)

^b Mean value±S.D., *n*=3

Table 4 Determination of fomes officinalis ames samples

Sample	Value obtained ($\mu\text{g g}^{-1}$)	
	As	Sb
1	0.561	0.742
2	0.552	0.756
3	0.563	0.759
4	0.545	0.734
5	0.531	0.728
6	0.533	0.767
RSD(%)	2.49	2.05

presence of pertinent ions. Thus, the influence of common interferences on the signals of $5.00 \mu\text{g l}^{-1}$ As and $0.5 \mu\text{g l}^{-1}$ Hg standard were investigated. The tolerance limits (mg l^{-1}), defined as interferential concentration subtracting the analyte signal by 10%, are presented as follows: Ca, Mg (1000); Fe, Zn (10); Cr, Te (4); Co (1.0); Ni, Hg(1.2); Sn, Cu(0.5); Sb, Se(0.3); Bi (0.1) and Pb (0.08) for As. Ca, Mg (1000); Zn (30); Cr, Te (4); Co, Ag (1.0); Ni, Fe (50); Sn, As, Cu(10); Se, Hg (7); Bi (5) and Pb (4) for Sb. The evaluation of interference demonstrated that the ions present in the majority of cases in samples influenced the measurement of As and Sb to an acceptable extent

Calibration Curves and Linear Ranges

The standard solution was determined in the best experimental conditions. The analytical results were presented in Table 2.

Detection Limit

The LOD values, calculated as three times the standard deviation of ten blank signal measurements divided by the slope of the calibration line. The detection limit of As and Sb was $0.03 \mu\text{g/L}$ and $0.08 \mu\text{g/L}$, respectively.

Accuracy and Precision of Method

In order to validate the method for accuracy and precision, a certified reference material GBW07605 (Chinese poplar leaves) was analyzed for each element. Each sample was prepared in duplicate and analyzed in triplicate (e.g. $n=6$). The results for each element are shown in Table 3. Excellent recoveries for all elements were obtained compared to the certified value.

Sample Analysis and Precision

All samples were determined by HG-AFS in the optimum experimental conditions. The determination of precision was six parallel measurements every sample. The analytical results were presented on Table 4.

Conclusions

Trace Arsenic and antimony were triumphantly simultaneous determined by an intermittent flow HG-AFS in fomes officinalis ames because of its high sensitivity, simplicity, and low costs, but most of such work has been element analysis. The method established in this paper provides high sensitivity, accuracy, precision and the merits of simultaneously determining the toxic elements of As and Sb by one measurement. The necessity of employing different methods for measuring As and Sb in sample can be avoided. Consequently it is rapid, simple and inexpensive.

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References

1. Qiao FX, Sun WH, Yan HY, Suo R, Li LX (2004) Simultaneous determination of trace arsenic and antimony in root of *Salvia miltiorrhiza bunge* by hydride generation-atomic fluorescence spectrometry. *J Hebei Univ* 24(2):163–167
2. Patricia CM, Cervera ML, Pastor A, de la Guardia M (2004) Cold vapour atomic fluorescence determination of mercury in milk by slurry sampling using multicommutation. *Anal Chim Acta* 506(2):145–153
3. Bian J, Sh W, Wang P, Fang ChG, Ma Y (1999) Determination of total arsenic by acid leaching-atomic fluorescence spectrometry. *Chin J Health Lab Technol* 9(4):270–273
4. Ipolyi I, Fodor P (2000) Development of analytical systems for the simultaneous determination of the speciation of arsenic [As(III), methylarsonic acid, dimethylarsinic acid, As(V)] and selenium [Se(IV), Se(VI)]. *Anal Chim Acta* 413(1):13–23
5. Xu BQ, Guo ShY, Bian J (2007) Simultaneous determination of bismuth and mercury in cosmetics by atomic fluorescence spectrometry. *Chin J Health Lab Technol* 17(4):742
6. He Y, Zheng Y, Ramnaraine M, Locke DC (2004) Differential pulse cathodic stripping voltammetric speciation of trace level inorganic arsenic compounds in natural water samples. *Anal Chim Acta* 511(1):55–61
7. Rahman L, Corns WT, Bryce DW, Stockwell PB (2000) Determination of mercury, selenium, bismuth, arsenic and antimony in human hair by microwave digestion atomic fluorescence spectrometry. *Talanta* 52(5):833–843