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Total antimony analysis by hydride generation-microwave plasma-atomic emission spectroscopy with applications

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Abstract

Antimony is widely used in industrial applications. In this study, we develop a method for total antimony analysis using a hydride generation-microwave plasma-atomic emission spectroscopy (HG-MP-AES) system equipped with a multimode sample introduction system (MSIS). Before analysis, antimony was reduced with potassium iodide and acidified with hydrochloric acid. The samples and a sodium tetrahydroborate/sodium hydroxide solution were infused into a spray chamber for hydride generation, MSIS. The limits of detection and quantification were 0.05 μg/L and 0.15 μg/L, respectively. Furthermore, semiconductor materials and blood samples have been analyzed in order to demonstrate the possible applications of this method. The total antimony content eluted from GaSb thin films in a pH 5 buffer agreed with the thin film structure. The spiked blood sample analysis showed that the recovery rate of antimony from the whole blood samples was 92.2 ± 1.67 %. Relative standard deviations for inter-day and intra-day assays of whole blood were 1.99 % and 5.31 %, respectively. The developed method was determined to have good accuracy and precision with the obtained values, and can be utilized for antimony analysis in the engineering and toxicological fields.

Keywords: Antimony; MP-AES; Hydride generation; GaSb thin film; Blood

1. Introduction

Antimony compounds naturally exist in the Earth's crust, predominately as Sb_2S_3 [1]. Compounds of antimony have been used as fire retardants, polymerization catalysts, and pigments [2]. Moreover, antimony sodium tartrate is used as an antiparasitic agent [3]. In the engineering field, Sb-based compound materials (e.g., GaSb, InSb, and CoSb) are predominantly applied in electrical and optical devices [4–6]. While antimony is widely used, its toxicity is well known; chronic exposure causes pneumoconiosis, abdominal pain, diarrhea, vomiting, lung tumors, and skin lesions called "antimony spots" [2]. Similar to arsenic, the toxicity of inorganic antimony is higher than that of organic antimony, and the trivalent form is ten times more toxic than the pentavalent form [7]. The drinking water quality guidelines laid down by the World Health Organization stipulate that the antimony content should not exceed 20 μg/L [8]. Therefore, the determination of antimony content in natural water sources and biological samples is imperative.

Total antimony analysis has been previously performed by graphite furnace atomic absorption spectrometry (GF-AAS) [9,10], hydride generation frame atomic absorption spectrometry (HG-FAAS) [11], and inductively coupled plasma (ICP) mass spectrometry [12–15]. Microwave plasma-atomic emission spectrometry (MP-AES) is a recently

introduced elemental analytical technique, which allows for multi-element analysis by recording the signals for different wavelengths in a sequential mode. Recently, MP-AES has been developed for the elemental analysis of foods, wines, fuel, geochemical samples, and bio-sludge samples [16-21]. MP-AES uses nitrogen plasma, which has a lower flame temperature (5000 K) compared to argon plasma (8000-10000 K), which is used in other elemental analysis techniques [20]. Due to the lower temperature, spectral interferences are less consequential, and atomic spectral lines have greater clarity [21]. Moreover, the operating cost is reduced, as nitrogen gas is more economical for generating plasma [22]. MP-AES offers better detection limits over a broader range of elements than HG-FAAS and has comparable limits to ICP-AES [23].

In this study, our approach was to develop a method for total antimony analysis by using hydride generation-microwave plasma-atomic emission spectroscopy (HG-MP-AES). HG has previously been used to measure metalloids, such as arsenic, selenium, antimony, and bismuth [24–36]. Conventional HG is performed using a hydride vapor generator. However, in this study, HG was conducted using a multimode sample introduction system (MSIS) as a spray chamber for HG, which was connected to an MP-AES instrument (Fig.1). The utilization of MSIS allows for a limit of detection (LOD) of the target hydride-forming element that is 100 times lower than seen for conventional

nebulization [37, 38], and the sample solution and hydride generation reagent can react at a rough-surfaced cone, which enables good mixing and fast gas-liquid separation [39]. To our knowledge, studies on total antimony analysis by HG-MP-AES with an MSIS are limited [39], and not enough research has been carried out in this area. This paper aims to develop a method for total antimony analysis by HG-MP-AES with an MSIS, and to apply this technique to semiconductor materials and blood samples analysis.

2. Materials and methods

2.1. Reagents

All reagents used in this study were of analytical grade. Concentrated nitric acid, 30 % hydrogen peroxide, concentrated hydrochloric acid (HCl) (60 %), potassium iodide (KI) (99.5 %), sodium tetrahydroborate ($NaBH_4$) (99.5 %), sodium acetate (98.5 %), sodium hydroxide (NaOH) (97.0 %), and antimony standard solutions (Sb 1000 mg/L) were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). The mixed standard for water quality analysis (DWS-3) was purchased from GL Sciences Inc. (Tokyo, Japan). Milli-Q water (> 18 mΩ, Merck Millipore, Burlington, USA) was used for the dilution of the standard solutions and other reagents.

2.2. Total antimony analysis by HG-MP-AES

The total antimony concentration was determined by HG-MP-AES using an Agilent 4200 MP-AES (Agilent Technologies, Santa Clara, USA) system coupled to an MSIS (Agilent Technologies, Santa Clara, USA). Parameters for antimony determination are shown in Table 1. Before analysis, antimony species in the calibration standards and samples (2.5 mL) were reduced with 20 % KI (500 µL), and acidified with 1 N HCl (2 mL) for at least 30 min. The reduced samples and the freshly prepared $NaBH_4$/NaOH solution (3 % w/v; 0.2 % w/v, respectively) were infused into the spray chamber for hydride generation (MSIS) using a peristaltic pump. The unused sample line to the spray chamber was blocked (Fig.1). The instrument detected antimony as gaseous antimony trihydride (stibine, SbH_3).

2.3. Determination of antimony content released from GaSb thin films

GaSb thin films (n = 4) were prepared by RF magnetron sputtering (HSR-351L, Shimadzu Industrial Systems Co., Ltd., Otsu, Japan) at 600 °C for 30 min on a quartz substrate (10 mm × 10 mm × 0.5 mm thick) under an Ar atmosphere at 0.5 Pa. The Ga content x in the Ga_xSb_{1-x} thin films was 0.6, and the film thickness was 393 nm. Detailed properties of the film have been reported in our previous studies [40, 41]. To assess the release of Sb from GaSb thin films, each film was immersed in 0.1 M of pH 5 sodium acetate buffer (1.5 mL) and incubated at 30 °C for 42 days. On day 1, 500 µL of the

immersion solution was removed and diluted with 1 N HNO_3 (4.5 mL), and the same volume of 0.1 M pH 5 sodium acetate buffer was added to the test tubes. On days 3, 5, 7, 14, 21, and 42, an aliquot (500 μL) was removed and acidified as on day 1. The GaSb thin film soaking procedure was performed in quadruplicate to ensure repeatability and allow standard deviations to be calculated.

2.4. Blood sample preparation

A whole blood sample from the author (0.5 mL) was digested in 2.5 mL of concentrated HNO_3 by heating at 65 °C for 1 h using the heating block acid digestion system DigiPREP Jr (GL Sciences, Tokyo, Japan). After adding 1.0 mL of 30 % H_2O_2 to the digested sample, the mixture was heated at 95 °C for 1.5 h. To calculate the recovery percentage, 20 μL of antimony standard solution (1000 mg/L) was added to the digested sample and then diluted to 20 mL with Milli-Q water.

3. Results and Discussion

3.1. Optimization of the total antimony analysis by HG-MP-AES using an MSIS

The emission intensity depends on gas flow, sample flow rate, and microwave power. The optimum operational parameters and instrumental details are shown in Table 1.

As for sample pretreatment, acid concentrations of the calibration standards and samples are unified. To analyze total antimony, antimony species in the calibration standards and samples have to be pre-reduced to the trivalent form: 20 % KI was used for this purpose, and 1 N HCl was simultaneously added to the sample solution. The optimized ratio of sample solution:20 % KI:1 N HCl was 5:1:4, and the optimized reaction time was 30 min. The reduced samples and the 3 % $NaBH_4$/0.2 % w/v NaOH solution were infused into the MSIS using a peristaltic pump: samples were continuously reduced to create antimony trihydride (stibine, SbH_3) (Fig.1).

3.2. Method evaluation

Under the optimized condition, calibration standards were analyzed by HG-MP-AES equipment in conjunction with an MSIS. Spectra of antimony standard solutions over the range of 0–1000 μg/L are shown in Fig.2. A linear calibration curve was obtained (y = 53.658x, r = 0.99996) (Fig.3). The LOD and the limit of quantification (LOQ) were calculated according to the formula LOD = 3σ/S (in μg/L) and the formula LOQ = 10σ/S, respectively, where σ is the standard deviation from a blank after 10 measurements and S is the slope of the calibration curve. LOD and LOQ were found to be 0.05 μg/L and 0.15 μg/L, respectively.

To assess the accuracy of this procedure, the method was applied to a mixed standard used in water quality analysis (DWS-3). The standard, DWS-3 (Sb concentration = 20 mg/L) was diluted 30-fold. The obtained total antimony concentration was 93 %, which was in good agreement with the DWS-3 standard concentration. Precision was evaluated by parameters such as repeatability (intra-day) and intermediate precision (inter-day). The intra-day and inter-day assays were performed using the mixed standard solution. The relative standard deviations (RSDs) for the mixed standard solution of the inter-day and intra-day assays were 1.31 % and 1.91 %, respectively.

3.3. Applications of the developed method

3.3.1 Antimony analysis eluted from GaSb thin film

The developed method was applied to determine the total antimony eluted from GaSb thin film with excess Ga. The thin films were soaked in pH 5 buffer and incubated at 30 °C for 42 days. Aliquots were removed at specified time points for antimony measurements. A pH 5 buffer was selected as the immersion solution because GaSb is slightly unstable in this environment, which allows for the slow elution of gallium from the thin film [40]. The RSDs of the antimony concentrations of the 4 samples at each time point ranged from 1.08 to 1.68 %. Figure 4 shows the amount of antimony eluted per day

from GaSb thin films over 42 days in pH 5 buffer, and it can be seen that antimony drastically eluted during the initial 14 days. Excess gallium contained in GaSb thin films forms gallium clusters in the surface region [41]. In this elution test, the crystalline quality in the surface region deteriorated due to the melting of the gallium clusters: gallium has a low melting point of 29.8 °C. This deterioration is speculated to cause the drastic elution of antimony during the initial 7 days.

3.3.2. Analysis of blood spiked with antimony

The antimony analysis of human blood samples is significant in toxicological evaluations and medical research. Because blood contains high levels of organic matter and remarkable amounts of sodium, which may cause matrix interference, blood itself is a complex sample matrix [42]. Sodium is one of the most easily ionized elements, and it is well known as a common interferent in atomic spectrometry. It is reported that MP-AES has relatively low interference, due to the inert nature of nitrogen plasma and the high temperature [43]. In the present study, the matrix effect of blood samples was investigated. Antimony spiked blood samples (0.5 mL and 1.0 mL) were digested with 2.5 mL concentrated HNO_3 and 1.0 mL of 30 % H_2O_2, and diluted to 20 mL, after which their antimony concentrations were determined. The antimony concentration of the 1.0

mL blood sample was found to be one-half of that seen for the 0.5 mL sample (data not shown), presumably due to matrix interference. This can be prevented by proper decomposition of organic matter and sample dilution. Thus, optimal digestion conditions were established, with a sample volume of 0.5 mL being digested in 2.5 mL HNO_3 at 65 °C for 1 h. After adding 1.0 mL of 30 % H_2O_2 to the digested sample, the mixture was heated at 95 °C for 1.5 h. The digested sample was then diluted to a volume of 20 mL.

The spectra of unspiked blood samples and those spiked with antimony are shown in Fig.5. The recovery of antimony-spiked whole blood was determined to be 92.2 ± 1.67 %. Intra-day and inter-day assays were performed with the antimony-spiked whole blood. The RSDs corresponding to the inter-day and intra-day assays for whole blood were 1.99 % and 5.31 %, respectively (Table 2).

3.4. Comparison of the analytical features of the present method with those of other published methods

The proposed method was compared with those in previously reported works using HG-MP-AES and HG analytical atomic spectrometry for antimony determination, and the results are summarized in Table 3. The LOD of the present method is comparable to nanoparticle-assisted MSIS-MP-AES, and superior to HG-AAS without pre-

concentration and HG-AFS. The RSD of the present method is lower than those of almost all of the previously reported methods. In the present study, a method of total antimony analysis with good analytical features, low running costs, and easy operation has been established.

4. Conclusion

In this study, a method for total antimony analysis by HG-MP-AES with an MSIS was developed. A linear calibration curve was obtained from 0 to 1000 μg/L, and the LOD and LOQ were determined to be 0.05 μg/L and 0.15 μg/L, respectively. The accuracy and precision were determined to be good. To investigate the stability of Sb-based thin films, solutions eluted from GaSb thin films with excess gallium were analyzed using the developed method. As a result, a tendency for antimony elution was observed, which was in agreement with the structure of the thin films. Moreover, this method was applied to blood sample analysis. The recovery rate of antimony-spiked whole blood samples was 92.2 ± 1.67 %. Hence, we believe that the developed method can be utilized for antimony analysis in the engineering and toxicological fields.

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Conflict of interest

There are no conflicts of interest to declare.

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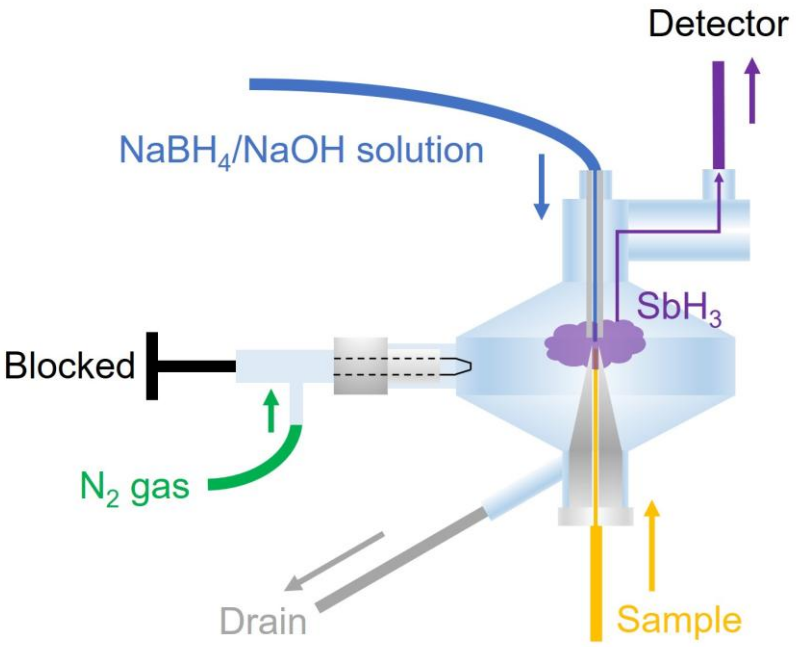

Fig.1. Illustration of the multimode sample introduction system (MSIS) used with the hydride generation-microwave plasma-atomic emission spectrometer.

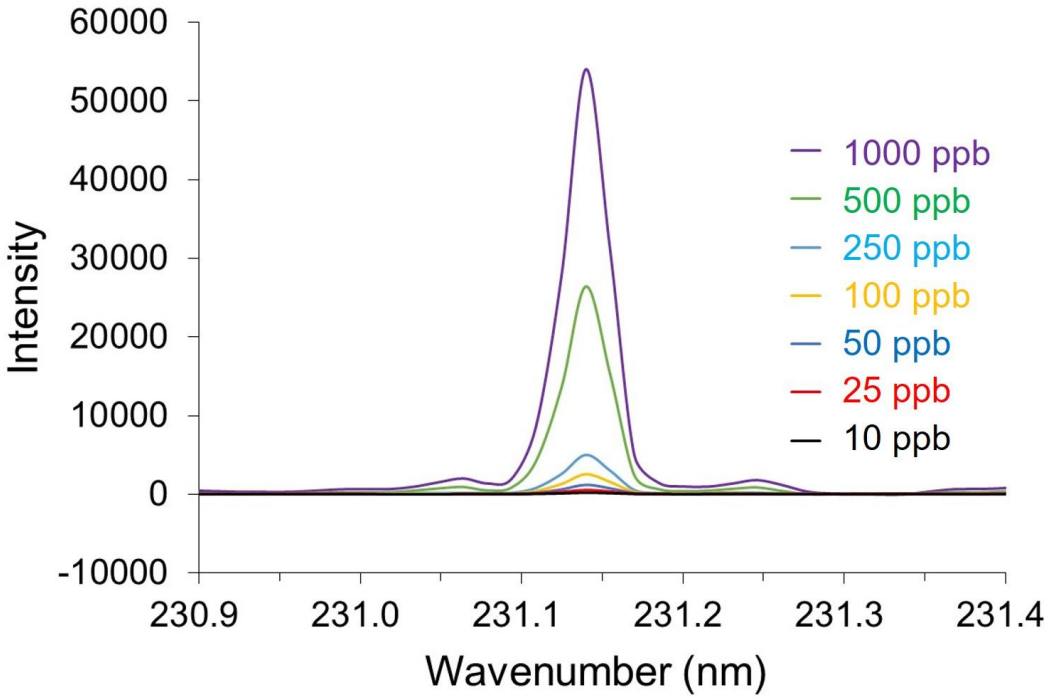

Fig.2. Spectra of the antimony calibration standard measured at 231.147 nm, at concentrations ranging from 10 to 1000 μg/L.

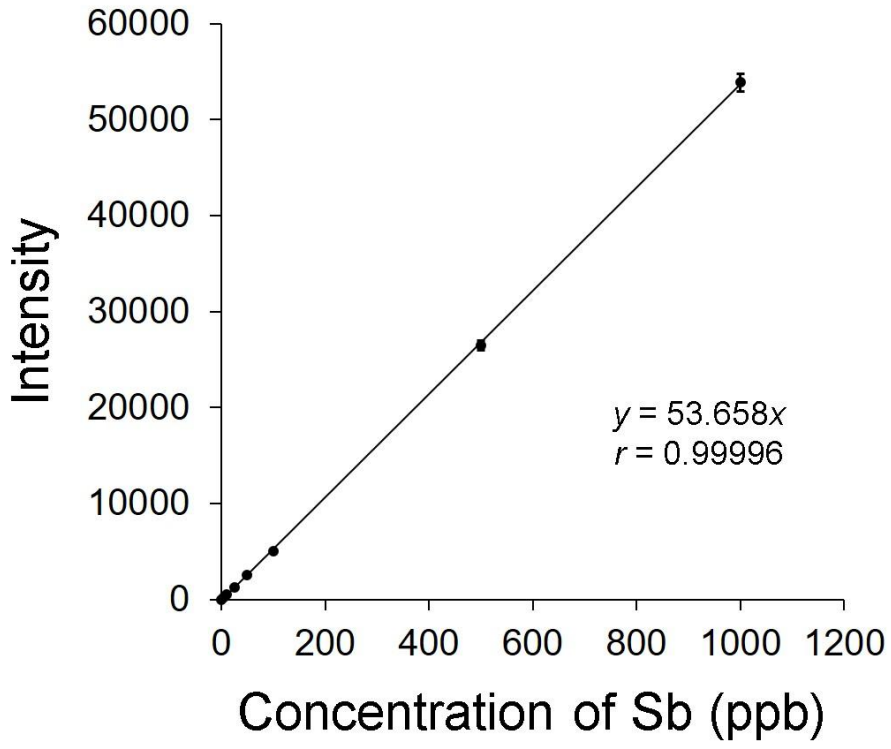

Fig.3. Calibration curve for total antimony determination by hydride generation-microwave plasma-atomic emission spectroscopy with a multimode sample introduction system.

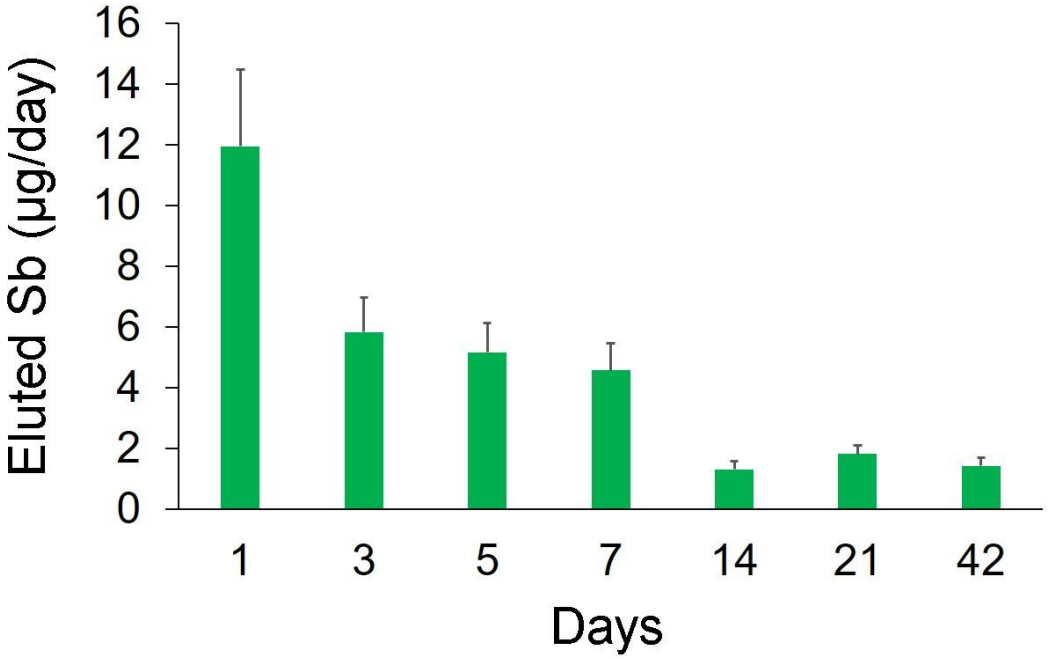

Fig.4. Antimony eluted per day from GaSb thin films in a pH 5 buffer measured at intervals over 42 days. Data is expressed as the mean ± standard deviation of four independently replicated sets of results.

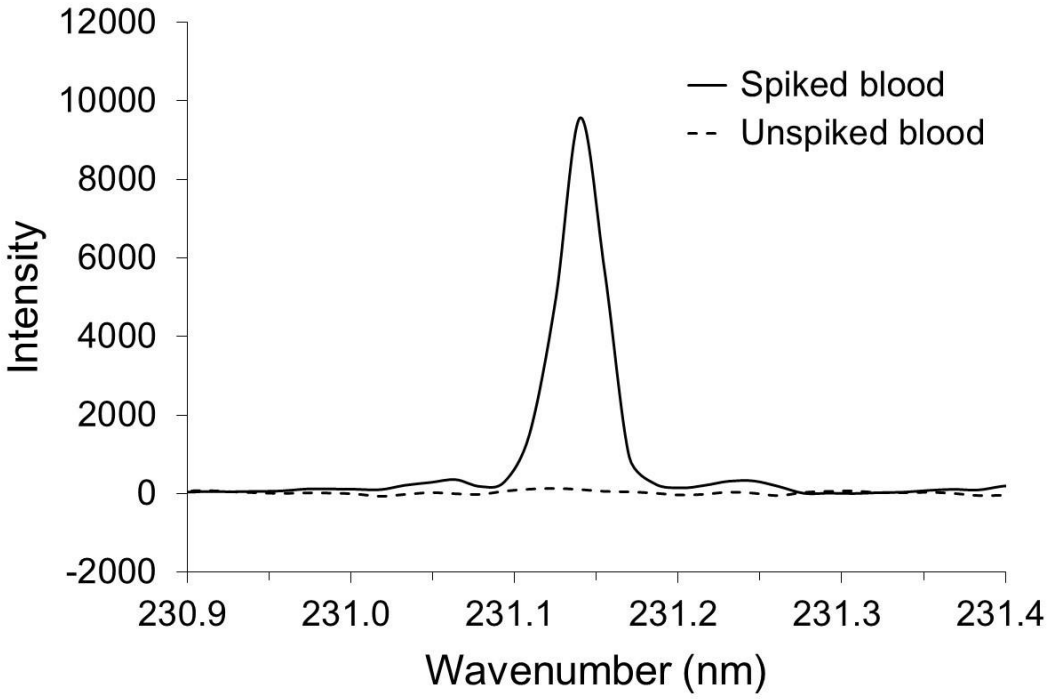

Fig.5. Spectra of a blood sample spiked with antimony and an un-spiked blood sample as measured at 231.147 nm.

Table 1. Parameters for antimony detection using an Agilent 4200 microwave plasma-atomic emission spectrometer (MP-AES) system coupled to a Multimode Sample Introduction System (MSIS)

Parameter	Setting
Sb wavelength	231.147 nm
Nitrogen gas supply	Nitrogen gas cylinder
RF Power	1.20 kW
Plasma flow	12.00 L/min
Auxiliary flow	0.70 L/min
Torch I.D.	1.80 mm
Nebulizer	Sea spray
Chamber	MSIS
Sample tube	Black/Black
Reduction tube	Black/Black
Drain tube	Black/White
Pump speed	20 rpm
Stabilization time	20 s
Read time	20 s
Repeat	3 times
High-speed pump during sample uptake	OFF

Table 2. Recovery and precision of antimony in a blood sample spiked with antimony

Sample volume (μL)	N	Sb added (μg/mL)	Sb found (μg/mL)	Recovery (%)	RSD of assay	
					Intra-day (%)	Inter-day assay (%)
500	3	20	18.4 ± 0.33	92.2 ± 1.67	1.99	5.32

RSD: relative standard deviation

Table 3. Comparison of total Sb determination methods using HG-MP-AES and HG-analytical atomic spectrometry

Sample	Detection method	Preconcentration/ extraction method	LOD[a] (μg/L)	RSD[b] (%)	Recovery (%)	Reference
GaSb thin films, whole blood	MSIS-MP-AES[1]	-	0.05	1.99	92.2	This study
Standard solution	Nanoparticles-assisted MSIS-MP-AES	-	0.05	1.50	-	Kiryakova et al., (2019) [39]
Water	HG-AAS[2]	-	0.3	0.4	98.8-103.7	Neri et al., (2015) [1]
Soil samples	HG-AAS	-	0.7	8.00	-	Matusiewicz et al., (2008) [30]
Water and food	HG-AAS	UA-CPE[6]	0.04	1.8-5.3	98-99	Altunay et al., (2016) [44]
Fish muscle tissue	HG-AAS	-	0.8	4.32	-	Silva Junior et al., (2017) [45]
Water and food	HG-AAS	DES-VAME[7]	0.02	2.7	96.2	Altunay et al., (2019) [46]
Bovine liver, pig kidney	FI-HG-AAS[3]	-	0.02	4.1-20	85-110	Krachler et al., (1999) [31]
Water	FI-HG-AAS	SPE[8]	0.001	2.1-2.4	98.1-103	Londonio et al., (2016) [47]
Environmental samples	HR-CS-ET-AAS[4]	MSPE[9]	0.003	2.2-2.9	95-105	Cárdenas Valdivia et al.,(2018) [32]
Hair samples	HG-AFS[5]	-	0.28	2.8	92.2-110	Cardozo et al., (2016) [48]
Soil samples	HG-AFS	-	0.9	3.2	90-116	Silva Junior et al., (2017) [49]
Standard solution	HG-AFS	-	0.04	4.1	-	Chen et al., (2018) [50]

[1]Multimode sample introduction system-hydride generation-microwave plasma-atomic emission spectroscopy

[2]Hydride generation-atomic absorption spectrometry

[3]Flow injection-hydride generation-atomic absorption spectrometry

[4]High resolution continuum source electrothermal atomic absorption spectrometry

[5]Hydride generation-atomic fluorescence spectrometry

[6]Ultrasonic-assisted cloud point extraction

[7]Eutectic solvent based vortex assisted microextraction

[8]Solid phase extraction

[9]Magnetic solid phase extraction

[a] Limit of detection

[b] Relative standard deviation