

Simultaneous determination of arsenic, antimony, selenium and tin by gas phase molecular absorption spectrometry after two step hydride generation and preconcentration in a cold trap system

Susana Cabredo ^a, Javier Galbán ^{b,*}, Jesús Sanz ^a

^a *Chemistry Department, Analytical Chemistry Section, University of La Rioja, Logroño-26001, Spain*

^b *Analytical Chemistry Department, Faculty of Sciences, University of Zaragoza, Zaragoza-50009, Spain*

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Abstract

A cold trap system for the simultaneous determination of arsenic, antimony, selenium and tin by continuous hydride generation and gas phase molecular absorption spectrometry is described. The hydride generation is carried out in two steps; first, tin hydride is generated at low acidity and second, arsenic, antimony and selenium hydrides are formed at higher acidity. All the hydrides are collected in a liquid nitrogen cryogenic trap and transported to the flow cell of a diode array spectrophotometer, where molecular absorption spectra are obtained in the 190–250 nm range. Five calibration solutions containing arsenic, antimony, selenium and tin are solved using multiple linear regression analysis. Tests are performed in order to extend the same manifold to other hydrides but no signals are obtained for bismuth, cadmium, lead, tellurium and germanium. Under the optimum conditions found and using the wavelengths of maximum sensitivity (190, 198, 220 and 194 nm), the analytical characteristics of each element are calculated. The detection limits are 0.050, 0.020, 0.12 and 1.1 $\mu\text{g ml}^{-1}$ and the RSD values are 3.7, 3.1, 3.5 and 3.0% for As, Sb, Se and Sn, respectively. The method is applied to As, Sb, Se and Sn determination in natural spiked water samples. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Simultaneous determination; Gas phase molecular absorption spectrometry; Cryogenic preconcentration; Hydrides

1. Introduction

The adaptation of a preconcentration step to the hydride generation (HG) process has been

extensively developed. When acid–metal reducers were used initially, this step was necessary because hydride generation was slow; preconcentration is still used nowadays to improve sensitivity. Preconcentration can be performed at room temperature [1,2] or at low temperature (mainly using liquid nitrogen) [3–5]. Cryogenic traps are

* Corresponding author. Tel.: +34 76 761292; fax: +34 76 671292; e-mail: jgalban@msf.unizar.es

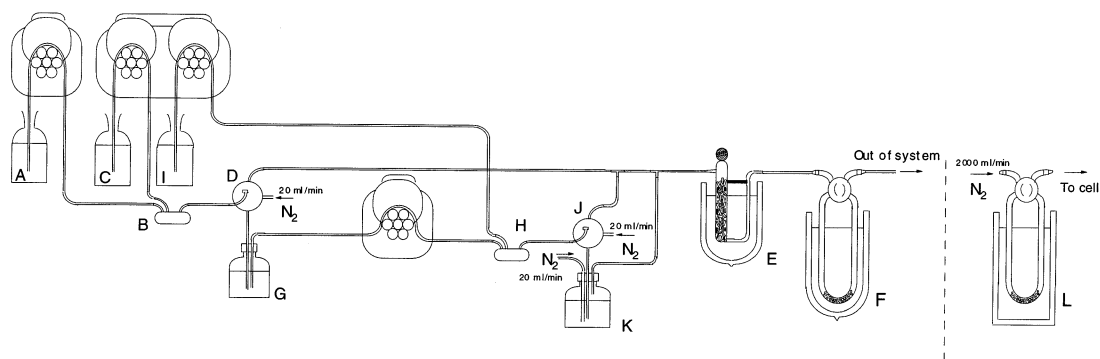


Fig. 1. Manifold used for simultaneous generation of As, Sb, Se and Sn hydrides. (A) sample solution at 35 ml min^{-1} containing As, Sb, Se and Sn in 0.05 M HCl ; (B) first generator; (C) $4\% \text{ NaBH}_4$ at 4 ml min^{-1} ; (D) first gas-liquid separator; (E) water trap (an ice and salt bath at $\approx -10^\circ\text{C}$); (F) hydrides trap (liquid nitrogen); (G) closed vessel; (H) second generator; (I) 2 M HCl solution at 4 ml/min ; (J) second gas-liquid separator; (K) third gas-liquid separator; (L) hot water bath at $\approx 80^\circ\text{C}$.

now the most common. Very useful information about hydride generation and preconcentration in a cold trap is provided by Dedina [6,7].

A survey of the literature indicates that there are not many papers describing analytical methods to determine four or more hydride-forming elements simultaneously. The difficulties result from the interelement interferences and the different oxidation states involved, which affect the generation kinetic. One of the more widely used techniques for simultaneous determination (without the preconcentration step) is HG-Induced Coupled Plasma-Atomic Emission Spectrometry (HG-ICP-OES), which has been used for arsenic and antimony [8–10], arsenic and lead [11], arsenic, antimony and selenium [12–15], arsenic, antimony and bismuth [16] or arsenic, antimony, bismuth, selenium and tin [17]. Speciation analysis is also possible, for example, As(III) and As(V) [18]. Sensitivity is good, but the cost of such equipment compared with other techniques has prevented it from becoming commonplace in analytical laboratories. A preconcentration system can also be combined with HG-ICP-OES [19]. Atomic absorption spectrometry is another technique which is widely used for speciation analysis of hydride-forming elements, such as arsenic [20] or tin [21].

In the last few years, we have studied in depth the analytical possibilities of Gas Phase Molecular

Absorption Spectrometry (GPMAS) for the determination of 1, 2 or 3 compounds (which have been recently reviewed [22]), mainly hydride forming elements and as a detector in gas chromatography [23]. In all those previous papers, the volatilization conditions for all the elements composing the mixtures have been the same. In this paper, we have tried to approach a new problem: the simultaneous determination of a mixture of elements in which different volatilization conditions have to be used. As a result, we have solved mixtures of arsenic, antimony, selenium and tin by GPMAS combined with a robust direct multivariate calibration method.

2. Experimental

2.1. Apparatus

All measurements were performed by using a Hewlett-Packard model HP 8451A diode-array spectrophotometer furnished with a quartz flow cell of 1 cm path length (Hellma 174 QS) and equipped with a keyboard HP98155A (Hewlett-Packard), a floppy disk drive for bulk data storage (Hewlett-Packard HP9121) and a graphics plotter (HP7475A).

For mathematical treatment, a Hewlett-Packard Vectra microprocessor with Eureka[®] software was used.

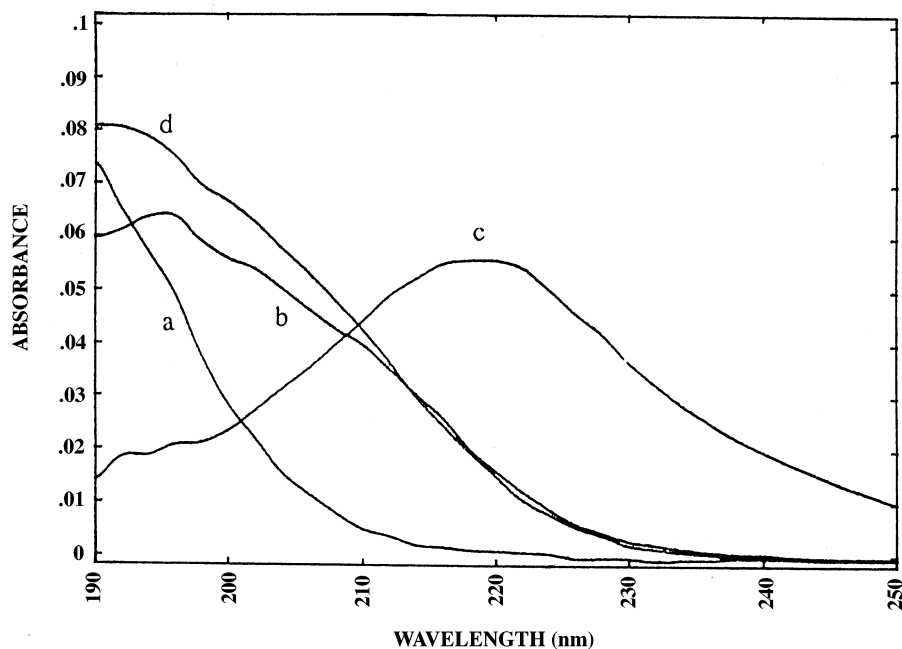


Fig. 2. Molecular absorption spectra in the gas phase of As (a), Sb (b), Se (c) and Sn (d) hydrides.

Reagents were pumped using two Masterflex peristaltic pumps, models 7518-10 and 7016-20 (Cole Parmer, Chicago, IL 60648) and one peristaltic pump model MS-4 Reglo (Ismatec S.A., Spain).

2.2. Reagents

All reagents used were of analytical grade quality. Doubly distilled water was used.

- Stock arsenic solution, 1000 mg l^{-1} , prepared by dissolving As_2O_3 (Merck) in 5 M NaOH, neutralizing with 5 M HCl and diluting with 0.5 M HCl.
- Stock antimony solution, 1000 mg l^{-1} , prepared by dissolving potassium antimony (III) oxide tartrate hydrate extra pure (Merck) in water and acidifying to 0.5 M with respect to HCl.
- Stock selenium solution, 1000 mg l^{-1} , prepared by dissolving extra-pure selenium metal (Merck) (1 g) in the minimum volume of 60% (w/w) HNO_3 and evaporating the solution nearly to dryness. Doubly distilled water (2 ml)

was added and the solution evaporated nearly to dryness (this was repeated twice). The residue was subsequently diluted to 1 l with 10% (v/v) HCl.

- Stock tin solution, 1000 mg l^{-1} , prepared by dissolving SnCl_2 (Merck) in diluted HCl.
- Concentrated HCl 1.19 g ml^{-1} and 35% (w/w) (Carlo Erba).

Working standards were prepared by serial dilution of the stock solutions with distilled water, immediately before use.

- Aqueous solutions of NaBH_4 (Merck) were prepared immediately before use. The same solution can be used for three or four measurements. By dissolving the NaBH_4 in water, the acidity can be controlled better than if dissolved in a basic medium.

2.3. System description. Recommended procedure

The system (Fig. 1) can be conveniently considered to consist of five sections: first generator (B), first gas-liquid separator (D), second generator (H), second gas-liquid separators (J and K), water

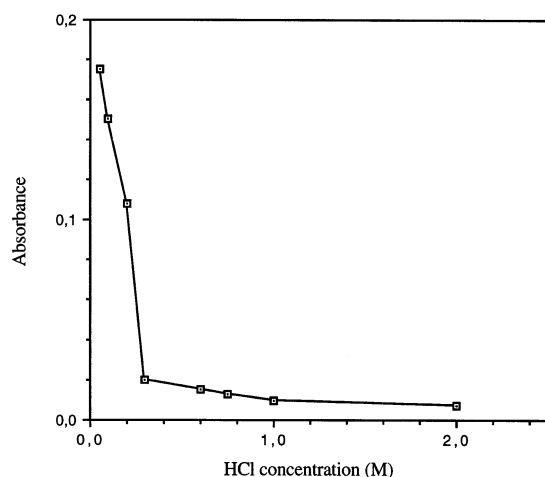


Fig. 3. Effect of HCl concentration on Sn hydride absorbance.

trap (an ice and salt bath at $\approx -10^{\circ}\text{C}$) (E) and the cryogenic trap (F). These components have been described previously [24].

The sample solution at 35 ml min^{-1} (A) containing arsenic, antimony, selenium and tin in 0.05 M HCl is mixed (B) with $4\% \text{ NaBH}_4$ at 4 ml min^{-1} (C). All the tin hydride and a low amount (between 10 and 20%) of arsenic, antimony and selenium hydrides are generated. The resultant gas–liquid mixture enters the first gas–liquid separator (D); the hydrides are transported by a carrier gas stream of nitrogen (20 ml min^{-1}) to the water trap (E) and finally to the hydride trap (F).

The liquid remaining at D goes to a hermetically closed vessel (G). The liquid is pumped into a generator (H), where it comes together with a 2

Table 1
Optimization of HCl concentration for the hydride generation of As, Sb and Se in the second generator

HCl concentration (M)	Absorbance		
	As	Sb	Se
3	0.0091	0.0098	0.0088
2.5	0.0100	0.0128	0.0094
2	0.0103	0.0158	0.0105
1.5	0.0085	0.0105	0.0068
1	0.0064	0.0085	0.0043

M HCl solution at 4 ml min^{-1} (I); arsenic, antimony and selenium hydrides are generated. The gas–liquid mixture is then passed through two gas–liquid separators (J and K); in J, a carrier nitrogen flow of 20 ml min^{-1} is used and in K, nitrogen gas is bubbled at 20 ml min^{-1} . The volatiles generated are also transported to the water trap (E) and hydride trap (F) consecutively.

After 5 min of generation and retention, the hydride trap is removed from the liquid nitrogen and left at room temperature for 5 min. Finally, it is placed in hot water ($\approx 80^{\circ}\text{C}$) for 1 min (L). In this way, the hydrides are volatilized and are then transported to the flow cell, with a nitrogen flow of 2000 ml min^{-1} . Molecular absorption spectra of the hydrides in the $190\text{--}250\text{ nm}$ range are obtained, which are subjected to multiple linear regression analysis.

3. Results and discussion

3.1. Previous tests

As has been mentioned, we had previously carried out the simultaneous determination of arsenic, antimony and selenium using continuous hydride generation with cryogenic preconcentration [24]. According to other authors [7] and our previous experience [25], tin forms its hydride under similar generation conditions. Based on this, the system employed for arsenic, antimony and selenium determination was tested for the simultaneous determination of the four elements (including tin). Unexpectedly, the results obtained were not satisfactory and high concentrations of tin were necessary to obtain a good analytical signal. As a consequence, we reconsidered the generation and trapping conditions for tin hydride and later the manifold design for continuous generation.

3.2. Continuous tin hydride generation: Optimization

Tin hydride presents a molecular absorption spectrum with a maximum at 194 nm (Fig. 2). The main parameters affecting tin hydride genera-

Table 2
Analytical characteristics for the simultaneous determination of As, Sb, Se and Sn

Element	Sensitivity (ml μg^{-1})	Quantification limit ($\mu\text{g ml}^{-1}$)	LD ($\mu\text{g ml}^{-1}$)	RSD* (%)
As	0.0950	0.050	0.050	3.7
Sb	0.1510	0.050	0.020	3.1
Se	0.0195	0.20	0.12	3.5
Sn	0.0030	1.5	1.1	3.0

* Obtained for $n = 8$.

tion are the concentration of the reducing agent (NaBH_4) and the acidity of the medium. The NaBH_4 concentration is very important, not only for a quantitative tin hydride generation but also to get a good preconcentration in the cryogenic trap. Different NaBH_4 concentrations from 1 to 7% (w/v) were tested. By using low NaBH_4 concentrations, a low quantity of hydrogen is also generated and the total gas flow passing through cryogenic trap is low. Nitrogen gas therefore, becomes trapped also; when the trap is submitted to room temperature, the nitrogen suddenly escapes from the valve and allows the volatiles to escape. NaBH_4 concentrations equal to or above 4% w/v avoid this problem. From the GPMAS point of view, the optimum acidity for tin hydride generation in the batch method is about 0.6 M [25]; however, using this continuous method, the results were very different. Hydrochloric acid at various concentrations was used in order to look for the optimum acidity; as can be seen in Fig. 3, the higher the concentration, the lower the absorbance value obtained. In addition, it was necessary to employ a low concentration (0.05 M) to obtain a good generation yield. We also tried generating the tin hydride by mixing a basic solution (0.1 M NaOH) containing tin and NaBH_4 with different concentrations of HCl (0.5, 0.05 and 0.025 M), but we did not observe better absorbance values. Given these points, the optimum acidity for tin hydride generation in our system was set at HCl equal to 0.05 M.

3.3. Continuous As + Sb + Se + Sn hydride generation: Optimization

The main problem which appears when 0.05

M HCl is used, is that the arsenic, antimony and selenium hydrides are not generated quantitatively. Therefore, if simultaneous generation and determination of the four hydrides is required, it is necessary to modify the system in order to change the acidity of the medium during the generation process. A new system was therefore designed (Section 2.3). As can be seen, a two step generation process is proposed, first at low acidity (principally generating tin hydride) and second, at high acidity (arsenic, antimony and selenium hydrides are generated quantitatively). Several tests were also made using the contrary mode, with prior generation at high acidity and later alkalization, but the results were not satisfactory.

Considering 0.05 M HCl as optimum for the first step, optimization of the HCl concentration for the second step was then carried out. Since selenium is the element which shows the lowest sensitivity in GPMAS, the study was undertaken with this element, although it was later tested for As and Sb, also showing an agreement with the results for selenium. The results obtained are shown in Table 1; it can be seen that the optimum acidity is 2 M HCl.

In order to investigate if the acidity in the second generator (H) affects the tin hydride generation, some studies were made using tin solution in 0.05 M HCl (solution A) and modifying the HCl concentration in the second generator; different solutions were used as solution I: doubly distilled water, 0.05 M HCl, 0.5 M HCl and 2 M HCl. The results proved that the tin hydride signal is independent of the acidity of solution I, showing that tin hydride is generated quantitatively in the first generator.

Table 3
Results for simultaneous determination of As, Sb, Se and Sn

Mixture	Real concentration ($\mu\text{g ml}^{-1}$)				Found concentration ($\mu\text{g ml}^{-1}$)			
	As	Sb	Se	Sn	As	Sb	Se	Sn
1	0.10	0.10	1.0	10.0	0.09	0.08	1.1	11.0
2	0.10	1.0	1.0	10.0	0.08	0.86	0.93	11.3
3	1.0	0.10	1.0	10.0	1.2	0.12	1.0	9.2
4	0.10	0.10	1.0	40.0	0.12	0.10	0.90	42.0
5	0.10	0.10	5.0	10.0	0.11	0.12	4.8	8.6

3.4. Analytical characteristics

Fig. 2 shows the gas-phase molecular absorption spectra of As, Sb, Se and Sn hydrides. It can be seen that the maxima appear at 190, 198, 220 and 194 nm, respectively.

Under the optimum conditions found and using the wavelengths of maximum sensitivity, the analytical characteristics of each element were calculated. Table 2 shows the sensitivity (the slopes of the calibration graphs), detection limits (the concentration corresponding to a signal of twice the standard deviation of the blank¹ signal), reproducibility (expressed as Relative Standard Deviation) and quantification limits (obtained experimentally) for each element.

It is necessary to note that the analytical figures of merit obtained for As, Sb and Se were slightly worse; so when simultaneous determination of these three elements was carried out [24], detection limits of 0.022, 0.015 and 0.065 $\mu\text{g ml}^{-1}$ and quantification limits of 0.050, 0.030 and 0.200 $\mu\text{g ml}^{-1}$ were obtained for As, Sb and Se respectively. However, this is compensated for by the possibility of carrying out the simultaneous determination of four elements.

3.5. Simultaneous determination

Resolution of five calibration solutions containing As, Sb, Se and Sn was carried out by using multiple linear regression analysis (MLR), based on resolving a system of ' n ' equations with four

unknowns (n = number of wavelengths used). In all cases, all the absorbance values were experimentally obtained in the 190–250 nm range. The optimum wavelength range to be used for MLR resolution (190–220 nm) was obtained by testing empirically different ranges. Table 3 shows a matching of the real mixture concentrations and the results obtained. RSD was in all cases better than 4% ($n = 4$).

3.6. Application

The method was applied for As, Sb, Se and Sn determination in drinking water. Following the procedure described previously, the samples were analyzed and in all cases, the endogeneous amounts of the elements were below the detection limit, so these elements were added to the drinking water samples. After As, Sb, Se and Sn addition, the samples were analyzed in quadruplicate by the proposed method and the results obtained are shown in Table 4. In all cases, the RSD was better than 4%.

3.7. Incorporation of other hydride-forming elements

Once the new system had been prepared for the simultaneous determination of As, Sb, Se and Sn, the incorporation of other hydride-forming elements, such as Bi, Cd, Pb, Ge and Te was tested.

3.7.1. Bismuth

It was not possible to determine bismuth using this methodology because its hydride is very unstable and the preconcentration is not effective

¹ The blank signal is obtained following the procedure, but using 0.05 M HCl as solution (A).

Table 4
Results for simultaneous determination of As, Sb, Se and Sn in drinking water samples

Sample	Added concentration ($\mu\text{g ml}^{-1}$)				Found concentration ($\mu\text{g ml}^{-1}$)			
	As	Sb	Se	Sn	As	Sb	Se	Sn
1	0.30	0.52	1.0	10.4	0.26	0.48	1.2	11.0
2	0.15	0.26	2.0	20.8	0.11	0.23	2.1	19.3

[26]. This was checked by using both molecular absorption spectrometry and atomic absorption spectrometry techniques. The bismuth hydride signal was obtained just before the nitrogen liquid trap; the signal disappeared after trapping in the cryogenic trap.

3.7.2. Cadmium and lead

When simultaneous determination of As, Sb and Se was performed, cadmium and/or lead showed a positive interference (Cd and/or Pb increase the hydride absorbance) on the signal. However, it was not possible to obtain a signal from hydrides of these elements in the absence of As, Sb and Se.

3.7.3. Germanium and tellurium

Based on our own experience [27,28], hydrides of these elements using a batch method are better generated from a basic medium. Nevertheless, considering the results obtained for tin hydride generation (in the batch method the optimum acidity is ten times higher than in the continuous method), a complete study using different Ge and Te hydride generation conditions from acid media was made. Several tests were made modifying the concentrations of HCl (0.5–6 M) and NaBH_4 (2–6%), and no signal was found in any case for germanium or tellurium.

In conclusion, we think that it will be possible to obtain a GPMAS signal from these elements in a continuous flow system (by using a different manifold), but that this will not be possible at the same time as investigating As, Sb, Se and Sn.

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