

Simultaneous determination of arsenic, antimony and selenium by gas-phase diode array molecular absorption spectrometry, after preconcentration in a cryogenic trap

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Abstract

This paper describes a method for the simultaneous determination of As(III), Sb(III) and Se(IV) by combining hydride generation and gas phase molecular absorption spectrometry. A system for continuous hydride generation has been designed and developed, based on the use of a double process of gas–liquid separation, and optimal compromise operation conditions for the three compounds have been found. After generation, the hydrides are collected in a liquid nitrogen cryogenic trap, and then evaporated and driven to the flow cell of a diode array spectrophotometer, in which the transient signals over the 190–250 nm wavelength interval are measured. Under the recommended conditions (sample flow: 35 ml min⁻¹, 0.5 M HCl; reductor flow: 4 ml min⁻¹ of 4% NaBH₄ solution) linear response ranges above 50 μg l⁻¹ for As(III), 30 μg l⁻¹ for Sb(III) and 200 μg l⁻¹ for Se(IV) are obtained with detection limits of 22 μg l⁻¹, 15 μg l⁻¹ and 65 μg l⁻¹, respectively. Multiwavelength linear regression equations were used for the simultaneous determination of the three elements in different synthetic samples, with good precision and accuracy and to study simultaneously the interference from different chemical species for the three compounds. Results were similar to those obtained by other techniques using hydride generation.

Keywords: Hydride generation; Antimony; Arsenic; Preconcentration; Selenium

1. Introduction

Hydride Generation (HG) has been widely used for many years [1] to determine elements which form hydrides; the great improvements in selectivity and sensitivity obtained justify investigations to develop the technique. These have produced continuous improvements such as electrochemical hydride generation [2] and new combinations with techniques like molecular chemiluminescence [3,4] or UV–visible molecular spectrometry (absorption [5–9], including

thermal lens [10], and emission [11]). One of the approaches that has been extensively developed is the adaptation of a preconcentration step to the generation process; initially, when acid–metal reductors were used, this step was necessary because hydride generation was slow, and nowadays it is still used to improve sensitivity. The preconcentration can be performed in two different ways: (a) at room temperature, through trapping and chemical reaction between the hydride and an organic reagent in solution, in which the hydride characteristics are lost, or (b) by physical preconcentration, so that it does not undergo chemical change.

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In the first case, it is traditional to use organic solutions of spectrophotometric reagents to facilitate determination by molecular absorption spectrometry. Although Ag–diethyldithiocarbamate is the best reagent for determination of As and Sb [12], reagents are available for every element which generates a hydride. This kind of reaction is not necessary for determination by atomic spectrometric techniques and thus, for example Yamaya et al. [13] retained selenium hydride in a HClO_4 – KMnO_4 solution prior to Se(IV) determination by atomic absorption spectrometry (AAS).

In the second case, the devices used to collect hydrides can be of different types but, at present, the most widely used are cold traps, based on liquid nitrogen cooling. The generation and collection process with these devices can be performed in two different ways, continuously or discontinuously. If the continuous mode is used, two separated flows of reductor (NaBH_4) and analyte (in acidic medium) are mixed; the generated hydride is separated from the liquid phase and preconcentrated in a liquid nitrogen trap, before determination of selenium [14], tin [15] or arsenic(III) and -(V) [16] by AAS.

If the discontinuous mode is used, the sample (acidic medium) is placed in a vessel and the reductor solution is added. The hydride is displaced with a carrier gas (N_2 or He) and collected in a cold trap. This procedure has been used in the generation of volatiles that need a longer reaction time, such as organometallic hydrides in speciation studies. Thus, arsenic [17], antimony [18], inorganic and methyl species of selenium [19], and tin [20] and organo-germanium species [21] have been determined by atomic spectrometric techniques.

The introduction of diode-array detection systems in UV–visible spectrophotometers has resulted in important improvements in their analytical capability, increasing their use in more selective studies by liquid chromatography or the development of gas phase molecular absorption spectrometry (GPMAS). This last technique has been used in the determination of Sb [5], Se [6] and Ge [7], after hydride generation, and sulphide [22] and ammonium [23] by H_2S and NH_3 generation. Its potential for speciation studies, (e.g., As(III) and As(V)) [24] or binary determinations of species (Bi and Se) [25] for which absorption spectra overlap, has been demonstrated. This paper shows that the use of hydride generation in a continuous mode, coupled to retention in liquid nitrogen, permits the use

of GPMAS for the simultaneous determination of As, Sb and Se down to trace levels. The mathematical data treatment permits determinations of these three elements, although their hydride absorption spectra show considerable overlap, with good precision and accuracy.

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 HP98155A keyboard (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.

Reagents were pumped using two peristaltic pumps, Masterflex Models 7518-10 and 7016-20 from Cole Palmer (Chicago, IL).

2.2. Reagents

All reagents used were of analytical grade quality. Doubly distilled water was used. Standard arsenic solution, 1000 mg l^{-1} , was prepared by dissolving As_2O_3 (Merck) in 5 M NaOH, neutralizing with 5 M HCl and diluting to volume with 0.5 M HCl. Standard antimony solution, 1000 mg l^{-1} , was prepared by dissolving potassium antimony(III) oxide tartrate hydrate (extra pure, Merck) in water and acidifying to 0.5 M in HCl. Standard selenium solution, 1000 mg l^{-1} , was prepared by dissolving extra-pure selenium metal (Merck) (1 g) in the minimum volume of 60% w/v HNO_3 and the solution was evaporated nearly to dryness. Doubly distilled water (2 ml) was added and the solution was evaporated nearly to dryness (this was repeated twice). The residue was subsequently diluted to 1 l with 10% v/v HCl. Working standards were prepared by serial dilution of the stock solution with distilled water immediately before use. A 4% w/v NaBH_4 aqueous solution was prepared immediately before use (Merck). Solutions containing potential interferents were prepared from chloride or nitrate salts.

3. System description. Procedure

Fig. 1 shows a schematic representation of the system used. The solutions are mixed well in the mixer (1) and enter the first gas–liquid separator (2) where the nitrogen carrier gas (20 ml min^{-1}) transfers the gaseous products into the water trap. The rest of the liquid goes to a second gas–liquid separator (3), through which N_2 gas is bubbled at 20 ml min^{-1} . The gas flow from this separator is carried into the water trap too. The water trap (4) is full of Raschig rings, and is immersed in an ice and salt bath (approximately -10°C). Finally, hydrides are retained in a glass U-tube (5) which contains a small quantity of glass spheres (diameter 2 mm), immersed in liquid nitrogen (-196°C). The liquid nitrogen trap is vented to the atmosphere. The Raschig rings and the small glass spheres are silanized.

The U-tube hydride trap is fitted with a four-way valve. This can be closed to retain compounds for temporary storage. After generation and trapping of a volatile hydride for 5 min, the U-tube is closed and removed from the liquid nitrogen for 5 more min. It is then introduced into hot water (approximately 80°C) for 1 min, after which the hydrides are transported to the continuous flow cell and placed in the spectrophotometer, with a nitrogen flow of 2000 ml min^{-1} .

To measure the transient signal, the spectrophotometer is programmed with a BASIC program that permits storage of molecular absorption spectra in the 190–250 nm range. The time interval between successive spectral plots is 0.2 s. All determinations of mixtures or standards are made at least in triplicate.

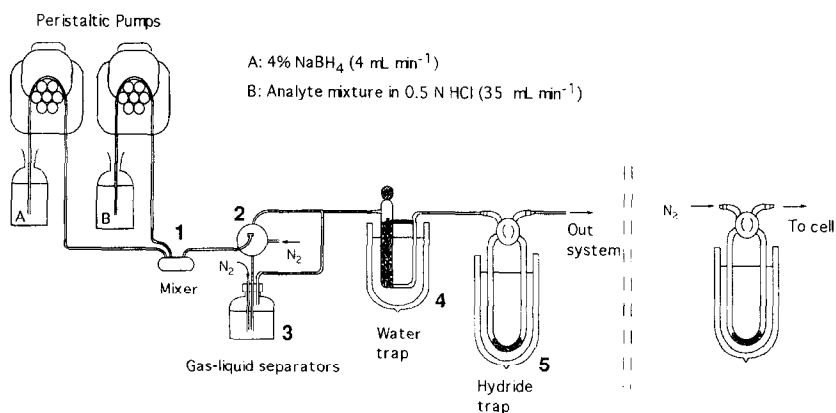


Fig. 1. Schematic diagram of the system (for explanation, see text).

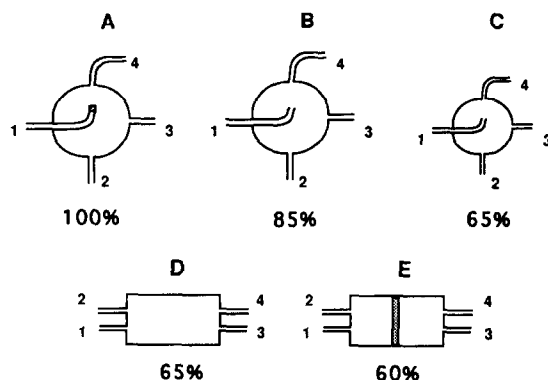


Fig. 2. Different gas–liquid separators used. (1) From mixer; (2) to waste; (3) nitrogen flow; (4) nitrogen + hydrides. Relative efficiencies for Se are shown.

To determine the As, Sb and Se contents in a mixture the maximum absorbance values for every wavelength from the 16 wavelength intervals between 190 and 220 nm (the spectral bandwidth of the spectrophotometer is 2 nm) are obtained. The computer then solves a series of simultaneous equations using the Eureka program.

4. Optimization of parameters

4.1. Instrumental

Selenium requires more drastic experimental conditions than As or Sb to generate its hydride and has the lowest sensitivity. Due to these characteristics most of the optimization studies were performed on this element, but later, verifications with As and Sb were made.

Gas–liquid separator

Different gas–liquid separators were designed in various sizes and types, as indicated in Fig. 2. This also shows the relative efficiency of the different separators compared to the spherical separator (A) with a porous glass tip. Besides giving a smaller efficiency, separator C resulted in too much water being transported with the hydrides. Cylindrical separators (D and E) were inconvenient to use.

In order to increase the separation effectiveness, the possibility of using two gas–liquid separators in series was studied, and different assays were made using different combinations of separators. The best results were obtained by coupling the spherical separator (A) with a bubbler (Fig. 1), which resulted in signal increases of 20% compared to the use of separator A alone.

Water trap

During the separation step, part of the liquid is nebulized and carried with the hydrides. Prior to the hydride retention in a liquid nitrogen trap, this liquid must be eliminated to avoid both suppression of hydride revolatilization and the transfer of water into the flow cell. In previous studies a multitude of water retaining materials have been used (drierite, molecular sieves, magnesium perchlorate, sulphuric acid, calcium chloride, ice baths or dry ice–acetone baths); in this paper the first drying agent used was calcium chloride. This gave acceptable results but had to be replaced many times and can result in partial hydride retention. The best results were obtained using an ice–salt bath, which offers an adequate temperature to retain the water without keeping back the hydrides. This effect was observed when a dry ice–acetone bath (ca. -70°C) was used.

Nitrogen flow

Nitrogen was used as carrier gas in two parts of the system. One flow carries the hydrides from the gas–liquid separators to the cryogenic trap and the other transfers them to the flow cell from the collector once they have been revolatilized.

Nitrogen flow rates in the separators (2 and 3) were studied between 20 and 100 ml min^{-1} for both separators in as wide a range as possible of flow-rate combinations. The results obtained are summarized in the following points. (1) Independently of the absolute value, both flows have to be equal to avoid problems

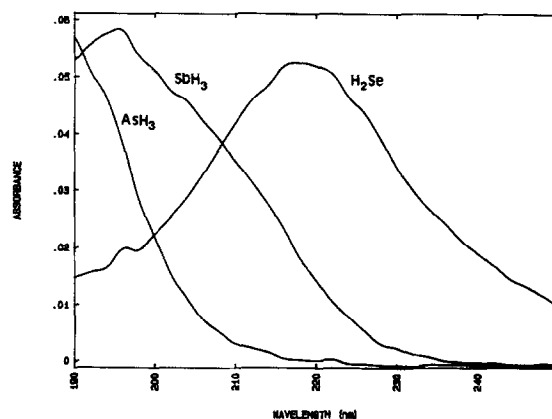


Fig. 3. Gas phase molecular absorption spectra of AsH_3 , SbH_3 and H_2Se .

of the gas reverse movement into the corresponding liquid phases, which produces redissolved hydride and less separation effectiveness. (2) The flow must be the lowest possible; for instance, if the flow decreases from 100 to 20 ml min^{-1} for every separator, the analytical signal increases by 400%. This is logical because the larger is the flow rate the lesser is the residence time of the hydride in the trap. (3) If the flow rate is $< 20 \text{ ml min}^{-1}$ in every separator, nitrogen is retained in the cryogenic trap. This nitrogen is later revolatilized, escaping from the valve and allowing hydride escape.

With respect to the nitrogen flow that transfers the hydride to the flow cell, it was observed that, as the flow was increased from 50 ml min^{-1} , bigger and more reproducible signals were obtained with an optimum of 2000 ml min^{-1} . At 50 ml min^{-1} , the signals gave a very good reproducibility but were smaller due to a hydride dilution effect in the carrier gas, as observed in previous studies [5–7].

Other parameters

Another aspect of the system that was studied is the distance between the mixer and the separator. Many distances were assessed but no differences in signal were observed. Thus it was proposed to use the minimum possible distance (3–4 cm). An exhaustive study was also performed of the time necessary for hydride revolatilization. The results indicated: (1) a stabilization time of the U-tube at room temperature was necessary before introduction into the hot water bath (if not, thermal shock sometimes shattered the trap); 5 min is optimal since over longer periods the signal decreases; (2) heating the U-tube after the 5 min of

Table 1
Variation of H₂Se absorbance with NaBH₄ concentration

NaBH ₄ conc. [% (w/v)]	Absorbance
2	0.0055
4	0.0094
6	0.0092
8	0.0081

stabilization was necessary; 1-min heating is optimal. If the measurement is performed without stabilization and heating, the signal decreases by ca. 50%.

4.2. Chemical

Although the generation conditions of these hydrides and their determination by GPMAS have been studied in previous papers [5,6,23] it has always been by discontinuous procedures where a great amount of H₂ gas arrived with the generated hydrides in the measurement cell. When cryogenic retention is used, H₂ is removed, which can alter the molar absorptivities of the hydrides. Besides this in coupling hydride generation with another techniques (usually AAS), the generation conditions change depending upon whether a continuous or discontinuous method is used. It is therefore necessary to study the main chemical parameters that affect the generation yield, viz., the medium acidity and NaBH₄ concentration.

NaBH₄ concentration

As observed in Table 1, the greatest signal appears at 4 or 6% NaBH₄. The decrease at larger concentrations is explained by the great quantity of hydrogen generated, which impedes the circulation of the carrier

Table 2
Analytical characteristics

Element	Sensitivity (ml μg ⁻¹)	Lower limit (μg ml ⁻¹)	Detection limit (μg ml ⁻¹)	R.S.D. ^a (%)	R.S.D. ^b (%)
As	0.1020	0.050	0.022	10.5	3.6
Sb	0.1720	0.030	0.015	10.1	3.8
Se	0.0307	0.200	0.065	11.0	4.0

^a Obtained for a concentration equal to a lower limit of the linear calibration range.

^b Obtained for a concentration five times larger than the lower limit.

Table 3
Results for simultaneous determinations

Mixture	Conc.	[As] (μg l ⁻¹)	[Sb] (μg l ⁻¹)	[Se] (μg l ⁻¹)
1	Real	50	50	500
	Found	32	59	620
2	Real	400	400	200
	Found	390	320	210
3	Real	200	200	2000
	Found	260	130	2000
4	Real	400	50	2000
	Found	400	59	2300
5	Real	2000	2000	5000
	Found	1700	1800	4500
6	Real	1000	50	500
	Found	800	61	510
7	Real	50	1000	500
	Found	37	1200	620

gas (N₂) through the system. The pressure gauge controlling the nitrogen flow indicated a pressure loss.

Acid

The amount of acid necessary for hydride generation was studied. For hydrogen selenide, the signal was not significantly modified over the range 0.5 to 2 M HCl, but decreased slightly at smaller or larger acid concentrations.

5. Analytical characteristics

Under the optimal instrumental and chemical conditions outlined in the Experimental section individual calibration studies were made for each element, using their wavelengths of maximum absorbance (Fig. 3) (190, 198 and 220 nm for As, Sb and Se, respectively). The sensitivity values obtained (slopes of calibration graphs) are indicated in Table 2. The same table gives the lower limits of the linear response range, the detection limits (based on twice the background standard deviation) and the reproducibility values (expressed as R.S.D.) obtained for two concentrations of each element, one the lower limit of the linear response range and the other to a selected higher concentration value.

The sensitivity was greater for As(III) and Sb(III) than for Se(IV); nevertheless these differences were not reflected in the detection limits, possibly because the maximum absorbance of Se(IV) appears in a spec-

Table 4
Results for interference study

Species	As	Sb	Se
Ca, Mg, Sr, Ba, Cr, Mn	4000 ^a	4000 ^a	1000 ^a
Fe	4000 ^a	4000 ^a	500
Hg	4000 ^a	4000 ^a	1000 ^a
Te	1000	1000	250
Pb	1000	1000	50
Sn	100	100	100
Ge	50	4000 ^a	1000 ^a
Ni	40	40	5
Co	40	40	5
Cu	100	100	10
Bi	200	20	50
Cd	2000	2000	500
Al, Zn	4000 ^a	4000 ^a	1000 ^a

^a Maximum ratio tested. Minimum ratio (w/w) giving 10% change in signal.

tral zone in which the baseline noise is smaller. The analytical parameters obtained are much better than those observed for discontinuous determinations.

6. Simultaneous determination

When a spectrophotometer with diode-array detector is used, simultaneous determination of the three hydrides in a mixture can be performed. The first procedure tested involved solving the following three equations with three unknown concentrations:

$$\text{Abs}_{190}^m = a_{190}^{\text{As}}[\text{As(III)}] + a_{190}^{\text{Sb}}[\text{Sb(III)}] + a_{190}^{\text{Se}}[\text{Se(IV)}]$$

$$\text{Abs}_{198}^m = a_{198}^{\text{As}}[\text{As(III)}] + a_{198}^{\text{Sb}}[\text{Sb(III)}] + a_{198}^{\text{Se}}[\text{Se(IV)}]$$

$$\text{Abs}_{220}^m = a_{220}^{\text{As}}[\text{As(III)}] + a_{220}^{\text{Sb}}[\text{Sb(III)}] + a_{220}^{\text{Se}}[\text{Se(IV)}]$$

where Abs_y^m is the measured absorbance of the mixture at each of the three wavelengths corresponding to the maximum absorbance of each hydride and a_y^i is the molar absorptivity of the individual hydride at the wavelength specified. The results obtained using this method on synthetic mixtures of As(III), Sb(III) and Se(IV) were quite imprecise and inaccurate, however.

In order to improve these results, a multi-wavelength method was applied. A system of n equations with three unknowns must be resolved, where n is the number of wavelengths used ($n > 3$) and the three unknowns are the concentrations of As, Sb and Se in the mixture. Absorbance values for every wavelength were obtained using a BASIC program. This program permits (i) obtaining the molecular absorption spectra in the range 190–250 nm while the hydrides are passing through the flow cell, (ii) storage of the absorbance values for every wavelength covering all spectra and (iii) selection of the maximum absorbance values for every wavelength and the numerical order of the spectrum in which these values appear.

In all cases it was observed that the absorbance maxima occurred at the same time for all wavelengths. Because of this, the three hydrides are volatilized and carried to the cell at the same time, so the reproducibility of the results is good.

In order to solve the equations, a mathematical program (Eureka) using an iterative procedure was used. Different wavelength intervals were assessed, but the best results were obtained using all wavelengths between 190 and 220 nm (16 equations, because the spectral bandwidth of the spectrophotometer is 2 nm). In Table 3 the results obtained for several mixtures of As, Sb and Se are shown. All results are the average of three determinations and the R.S.D. values were, in all cases, < 5%. The concentrations found agreed reasonably with the known values although some problems remain.

7. Interference study

The proposed method for the simultaneous determination of the three elements as outlined above, allows the simultaneous study of interference effects on the three species. Solutions containing As, Sb and Se and the potential interferent element were prepared. Each of these solutions was subjected to the generation and determination procedure and the concentrations obtained by this method were compared with the known values to assess the extent of interference. Table 4 indicates the minimum w/w ratios at which the concentration obtained differs by 10% from the known value. All experiments were performed in triplicate.

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