

1998

Flow injection determination of selenium by successive retention of Se(IV) and tetrahydroborate(III) on an anion-exchange resin and hydride generation electrothermal atomization atomic absorption spectrometry with in-atomizer trapping - Part 1. Method development and investigation of interferences

PE Carrero

JF Tyson

Follow this and additional works at: https://scholarworks.umass.edu/chem_faculty_pubs

 Part of the [Chemistry Commons](#)

Recommended Citation

Carrero, PE and Tyson, JF, "Flow injection determination of selenium by successive retention of Se(IV) and tetrahydroborate(III) on an anion-exchange resin and hydride generation electrothermal atomization atomic absorption spectrometry with in-atomizer trapping - Part 1. Method development and investigation of interferences" (1998). *Spectrochimica Acta Part B-Atomic Spectroscopy*. 1057.

Retrieved from https://scholarworks.umass.edu/chem_faculty_pubs/1057

This Article is brought to you for free and open access by the Chemistry at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Chemistry Department Faculty Publication Series by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.

Flow injection determination of selenium by successive retention of Se(IV) and tetrahydroborate(III) on an anion-exchange resin and hydride generation electrothermal atomization atomic absorption spectrometry with in-atomizer trapping

Part 1. Method development and investigation of interferences

Pablo E. Carrero¹, Julian F. Tyson*

Department of Chemistry, Box 34510, University of Massachusetts, Amherst, MA 01003-4510, USA

Received 29 June 1988; accepted 26 October 1998

Abstract

A sample solution was passed at 20 ml min⁻¹ through a column (150 × 4 mm²) of Amberlite IRA-410Stron anion-exchange resin for 60 s. After washing, a solution of 0.1% sodium borohydride was passed through the column for 60 s at 5.1 ml min⁻¹. Following a second wash, a solution of 8 mol l⁻¹ hydrochloric acid was passed at 5.1 ml min⁻¹ for 45 s. The hydrogen selenide was stripped from the eluent solution by the addition of an argon flow at 150 ml min⁻¹ and the bulk phases were separated by a glass gas-liquid separator containing glass beads. The gas stream was dried by passing through a Nafion® dryer and fed, via a quartz capillary tube, into the dosing hole of a transversely heated graphite cuvette containing an integrated L'vov platform which had been pretreated with 120 µg of iridium as trapping agent. The furnace was held at a temperature of 250°C during this trapping stage and then stepped to 2000°C for atomization. The calibration was performed with aqueous standards solution of selenium (selenite, SeO₃²⁻) with quantification by peak area. A number of experimental parameters, including reagent flow rates and composition, nature of the gas-liquid separator, nature of the anion-exchange resin, column dimensions, argon flow rate and sample pH, were optimized. The effects of a number of possible interferents, both anionic and cationic were studied for a solution of 500 ng l⁻¹ of selenium. The most severe depressions were caused by iron (III) and mercury (II) for which concentrations of 20 and 10 mg l⁻¹ caused a 5% depression on the selenium signal. For the other cations (cadmium, cobalt, copper, lead, magnesium, and nickel) concentrations of 50–70 mg l⁻¹ could be tolerated. Arsenate interfered at a concentration of 3 mg l⁻¹, whereas concentrations of chloride, bromide, iodide, perchlorate, and sulfate of 500–900 mg l⁻¹ could be tolerated. A linear response was obtained between the detection limit of 4 ng l⁻¹, with a characteristic mass of 130 pg. The RSDs for solutions containing 100 and 200 ng l⁻¹ selenium were 2.3% and 1.5%, respectively.

Keywords: Selenium; In-atomizer hydride trapping; Ion-exchange preconcentration; Solid phase hydride generation; Electrothermal atomization; Flow injection

* Corresponding author. Tel.: 00 1 413 545 0195; Fax: 001 413 545 4846; e-mail: tyson@chem.mass.edu.

¹ On leave from IVAQUIM (Venezuelan Andean Institute for Chemical Research), Faculty of Sciences, University of Los Andes, P.O. Box 542, Merida 5101-A Venezuela.

1. Introduction

Hydride generation sample introduction for atomic absorption spectrometry (HG-AAS) and for other

atomic spectrometric techniques has a number of advantages in the determination of selenium and other volatile hydride forming elements and the technique has become one of the most successful and convenient methods for the determination of such elements [1]. Currently, the most popular atomization source for hydride generation AAS is the heated quartz T-tube. The T-tube can be heated either by means of a flame [2,3] (usually an air–acetylene flame) or by an electric furnace [4,5]. Electrical heating offers the possibility of selecting an optimum atomization temperature for each particular element [3]. Some of the main problems associated with conventional hydride procedures are that the analyte hydrides are diluted by the co-evolved hydrogen and carrier gas, thereby decreasing the sensitivity of the determination, and that many hydrides are not efficiently atomized at the maximum temperature attainable in quartz tubes and therefore suffer from gas phase interferences [6].

The in-atomizer trapping methodology [6–15] has substantial advantages over conventional furnace or quartz tube techniques: large sample volumes, freedom from vapor phase interferences and high sensitivity. The technique also increases the relative detection power as a result of the in-atomizer analyte preconcentration and the HG procedure separates analyte from matrix species making the determination less prone to interferences and reducing the importance of background correction. Quartz tube atomizers require periodic reconditioning with HF solution – a tedious and potentially dangerous operation which is avoided when an electrothermal atomizer is used.

Currently methods using the in-atomizer trapping procedure suffer from a number of limitations. In previous work on hydride generation with in-atomizer trapping for determination of low concentrations of selenium by ETAAS, [16] we have found that detection limits were governed by impurities in the borohydride reagent. The ability of the in-atomizer trapping technique to use large sample volumes (larger than, say, 5 ml) could be limited in terms of the time required per analysis. For example, according to the manufacturer of the equipment used, [17] the time necessary to process 2 ml of sample is 80 s. Also, keeping the quartz capillary in the furnace for a longer period of time may result in a carry-over effect [15].

Tesfalidet and Irgum [18] and Narasaki et al. [19] showed that arsine could be generated by passage of an acidified sample through a column of anion-exchange material on which borohydride had been previously immobilized. In previous work [20] we found that the co-immobilization of selenium (as selenite) and borohydride on an anion-exchange resin followed by passage of acid to generate hydrogen selenide was the basis of a viable method for the determination of selenium by HGAAS with quartz tube atomization. Quantitative recovery of selenium from water samples was achieved.

In this article we describe developments of this procedure to allow (a) the preconcentration of selenium on the anion-exchange resin, (b) the separation of analyte from potentially interfering matrix compounds, (c) the use of ETAAS with in-atomizer trapping and (d) automation of the procedure using a FLAS 200 flow injection analyzer. These developments address some of the limitations of the procedure. For example a method based on the concept of the co-immobilization on an anion-exchange column of selenium and borohydride, which must be performed with an alkaline solution, will suffer interferences if the sample solution contains metals which precipitate from alkaline solution. Further, when selenium and borohydride were co-immobilized, the analytical signal of selenium strongly depended on the borohydride concentration [20]. The selenium signal decreased sharply as the borohydride concentration increased from 0.5% to 1.0% (m/v). Therefore, the preconcentration of selenium by coimmobilization with borohydride from a large sample volume may result in a sub-optimal amount of borohydride in the column. Successive retention of selenium and borohydride could not only avoid the problem of the precipitation of transition metals, but also allow the amount of sample and the amount of borohydride used, the blank contribution from this reagent could be decreased with a consequent improvement in the detection limit.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade,

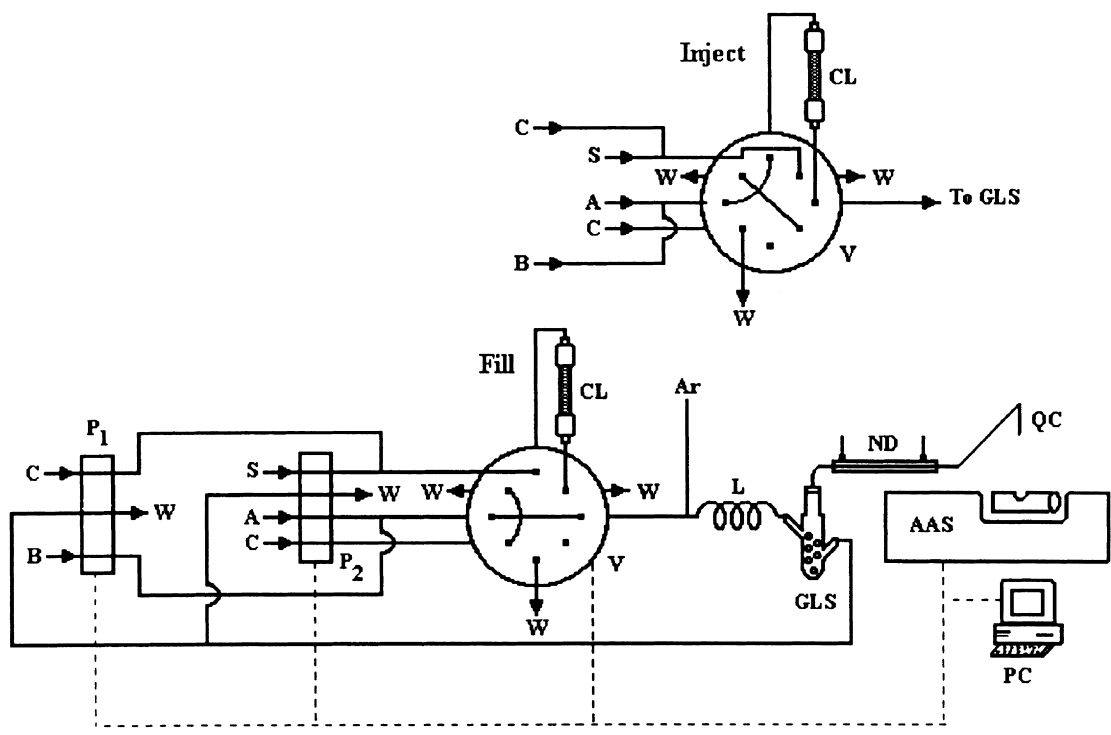


Fig. 1. Schematic diagram of the manifold and the instrumentation setup for selenium preconcentration and hydride generation from a solid phase with in-atomizer trapping. V, eight-channel (16-port) valve; P_{1,2}, peristaltic pumps of the FIAS-200 system; CL, column packing with strong anionic-exchange resin; L, stripping coil; ND, Nafion dryer; QC, quartz capillary; GLS, gas-liquid separator; PC, computer; AAS, 4100ZL atomic absorption spectrometer; C, purified water; B, sodium borohydride; A, hydrochloric acid; W, waste.

unless otherwise stated. Deionized distilled water was used throughout. All the laboratory materials were carefully cleaned before use by first washing with a neutral detergent solution and then rinsing with both distilled and deionized distilled water. A stock solution of 1000 mg l⁻¹ of selenite (SeO₃²⁻) (Fisher Scientific), from which working standard solutions were prepared daily by further dilution, was used. Sodium borohydride solution. 0.1% (m/v) in 0.05% (m/v) sodium hydroxide, was prepared just prior to use by dissolving 0.51 g of sodium borohydride (98% purity, Alfa) in 500 ml of sodium hydroxide solution 0.05% (m/v) (original solid from Fisher Scientific). Hydrochloric acid, 8 mol l⁻¹, was prepared by diluting 661 ml of concentrated hydrochloric acid (Fisher Scientific) to 1000 l with water. The resins used were Amberlite IRA-410 and Amberlyst A26 (Aldrich), which are strongly basic anion exchange resins with a styrene-divinylbenzene skeleton.

2.2. Apparatus

A Perkin-Elmer model 4100ZL atomic absorption spectrometer with a transversal heated graphite atomizer (THGA) and longitudinal Zeeman-effect background correction was used. The spectrometer was interfaced with a Digital 316sx PC computer, and programmed/controlled with the FIFU version of the Perkin-Elmer Gem software (v7.2.1). Standard THGA graphite tubes with integrated platforms (Perkin-Elmer, part No B300-0641) were pretreated with 120 µg of iridium following the procedure recommended by the manufacturer [17]. A Perkin-Elmer "system 2" electrodeless discharge lamp was used as a radiation source, with detection at 196.0 nm.

The flow injection manifold, shown in Fig. 1, was assembled on a Perkin-Elmer FLAS-200 unit, equipped with an eight-channel (16-port) switching valve. The manifold was constructed from Perkin-

Table 1
FIAS-200 manifold coils, tubing and flow rates (also see Fig. 1)

Parameter	Description
Stripping coil (L)	PTFE tubing 30 × 1 mm i.d.
Sample conduit	Tygon 2.06 mm id violet/ violet (double channel) 20.0 ml min ⁻¹ , 100 rpm P ₂
Purified water conduit	Tygon 1.14 mm id red/red 5.1 ml min ⁻¹ , 100 rpm P ₁
Acid conduit	Tygon 1.14 mm id red/red 5.1 ml min ⁻¹ , 100 rpm P ₂
Sodium borohydride conduit	Tygon 1.14 mm id red/red 5.1 ml min ⁻¹ , 100 rpm P ₁
Waste for the gas–liquid separator	Tygon 3.18 mm id white/ black 15.3 ml min ⁻¹ , 100 rpm P ₁

Elmer 1.0 mm i.d. PTFE tubing and Perkin–Elmer Chemifold flow injection fittings. The optimized parameters for the FLAS-200 manifold are given in Table 1. A Nafion[®] dryer, 30.5 cm long and 2.2 mm i.d. (Perma Pure, Model MD-250) was fitted to the gas transfer line. The PTFE capillary of the AS-71 graphite furnace autosampler was replaced by a quartz capillary, which was connected to the Nafion dryer. The column used (150 × 4 mm²) has been described previously [20]. A glass gas–liquid separator with

Table 2
Optimal operation conditions

<i>Spectrometer</i>	
Wavelength	196 nm
Spectral bandpass	2.0 nm (low)
EDL system 2 current	260 mA, modulated
Signal measurement	Peak area
Background correction	Zeeman-effect
Trapping temperature	250°C
Internal furnace gas flow during Trapping step	250 ml min ⁻¹
<i>On line preconcentration and hydrogen selenide generation</i>	
NaBH ₄ concentration	0.1% (m/c)
NaBH ₄ flow rate	5 ml min ⁻¹
HCl concentration	8 mol l ⁻¹
HCl flow rate	5 ml min ⁻¹
Stripping/carrier gas flow (argon)	150 ml min ⁻¹
Sample flow rate	20 ml min ⁻¹
Sample load time	60 s
Column size (length × i.d.)	150 × 4 mm
Resin	Amberlite IRA-410

glass beads (Perkin–Elmer part No B019-3772) was used.

2.3. Procedure

All of the experiments were carried out using the manifold shown in Fig. 1 under the optimal conditions shown in Table 2. The steps followed for selenium determination are summarized in Table 3 and Table 4. The column was cleaned between samples and standards by passing a solution of 2% (m/v) sodium borohydride in 0.1% (m/v) NaOH, followed by HCl 8 mol l⁻¹ and finally purified water through the sample conduit (valve in fill position) for 20 s each at a flow rate of 20 ml min⁻¹. The cleaning step was performed manually using the FLAS-control window of the Benchtop software. The cleaning step was not needed between replicate injections of the same sample or standard.

2.4. Method development

2.4.1. Gas–liquid separation

Three types of gas–liquid separators were used, namely, the glass device with glass beads (Perkin–Elmer, part No B019-3772), the modular ‘building block’-type device made from chemically resistant plastic (Perkin–Elmer, part No B050-7959), and a device constructed in-house from a 25-ml separating funnel [20]. The drains from all these devices were pumped. In the case of the separating funnel device, the drain pump rate was such that there was always 1–2 ml of liquid remaining in the funnel.

2.4.2. Removal of water vapor and droplets from the gas transfer line

The carry-over of vapor or droplets of reaction mixture, which contains water, acid, NaCl, Na₃BO₃, etc., into the graphite furnace results in serious problems in the trapping process. Therefore, the moisture in the gas transfer line must be removed before it reaches the graphite furnace. Two different systems were used to remove the moisture a Nafion dryer, 30.5 cm in length and 2.2 mm i.d. (Perma Pure, Model MD-250), and a glass tube, 150 mm in length and 4 mm i.d. Two PTFE reducing unions 1/4 × 1/8 in. (Cole-Parmer) fitted at either end of the glass tube were used to connect it to the transfer line. The glass tube was considered as a possibility for

Table 3

FIAS-200 program for selenium and BH_4 successive retention for selenium hydride generation with in atomizer trapping and ETAAS detection (see also Fig. 1 and text)

FIAS step	Time/s	Pump 1/ rpm	Pump 2/rpm	Valve position	Comments
Prefill	15	100	100	Inject	The sample conduit is flushed with sample solution; graphite tube is heated to the trapping temperature.
1	60	0	100	Fill	The sample is pumped through the column for the analyte retention; acid is pumped through the gas-liquid separator; purified water is pumped through the bypass in the valve to remove the acid
2	30	100	0	Fill	Purified water is pumped through the column, in order to flush interfering species present in the sample; sodium borohydride is pumped through the gas-liquid separator
3	60	100	0	Inject	Sodium borohydride is pumped through the column for BH_4 retention
4	30	100	0	Fill	Purified water is pumped through the column; sodium borohydride is pumped through the gas-liquid separator
5	8	0	0	Inject	Quartz capillary is placed into the graphite tube
6	45	0	100	Inject	Acid is pumped through the column and the selenium hydride is generated; sample is pumped to waste
7	8	0	0	Inject	Quartz capillary is moved out of the graphite tube
8	30	100	0	Fill	Start of furnace program; purified water is pumped through the column to remove the acid remaining in the column

Table 4

THGA program for selenium determination. Trapping temperature 250°C

Step no.	Temperature/°C	Ramp/s	Hold/s	Ar flow rate/ ml min ⁻¹	Read
1	250	1	15	250	
2	2000	0	5	0	Yes
3	2300	1	2	250	

removal of moisture as wetting of the interior of the larger diameter interior surface provided a mechanism for retention of drops of moisture. Dry air was used as purge gas for the Nafion gas for the Nafion dryer at a flow rate of 200 ml min^{-1} .

2.4.3. Column packing and dimensions

Two different strongly basic resins, Amberlite IRA-410 and Amberlyst A26, were packed in columns of various dimensions. Both resins have styrene-divinylbenzene skeletal structures, however Amberlite IRA-410 is a gel-type resin and Amberlyst A26 is a porous or macroreticular resin. The resulting columns were tested for selenium retention and subsequent hydride generation.

2.4.4. Parameter optimization

The multi-cycle alternating variable search method [21,22] was used for the optimization of the following parameters: the borohydride concentration, the time the borohydride solution was passed through the column, the HCl concentration, and the stripping/carrier gas flow rate. The figure of merit for the optimization process was maximum net (i.e. blank subtracted) peak area signal. Other parameters that were studied included the dimensions of the column, the nature of the anion-exchange resin, the flow rate of the borohydride solution, and the flow rate and pH of the sample solution.

The flow rate of the borohydride solution was varied from 1 to 10 ml min^{-1} for 0.1% (m/v) NaBH_4 and 60 s . At a flow rate of 5 ml min^{-1} , different amounts of BH_4^- were passed through the column by varying the concentrations of sodium borohydride within the range 0.01% – 0.5% (m/v) and the length of time that the reagent was passed through the column. The effect of the stripping gas was evaluated by varying the argon flow rate between 0 and 250 ml min^{-1} . To study the effect of the concentration of the acid used for the selenium hydride generation, two solutions containing 500 ng l^{-1} Se(VI) were prepared, one of which contained 10 mg l^{-1} of Cu^{2+} (added to study the effect of the HCl concentration in the prevention of interference by transition metals). The hydrochloric acid concentration was varied from 1 – 10 mol l^{-1} for each solution.

2.4.5. Effect of the pH of the sample

The acid dissociation constants of selenous acid (H_2SeO_3) are $\text{p}K_1 = 2.6$ and $\text{p}K_2 = 8.2$ [23]. As the retention of analyte depends directly on the amount of selenium present in the form of HSeO_3^- and SeO_3^{2-} , the sample has to be controlled. To study the effect of sample pH on the signal, 500 ng l^{-1} of Se(IV) solutions were prepared with pH values within the range 1 – 12 . The pH of the solution, measured, by a combination electrode and pH meter, was adjusted with HCl or NaOH solutions as required.

2.4.6. Effect of interferences

It is well-known that the hydride generation technique for selenium determination is susceptible to severe interferences caused by the presence of transition metals, mainly those of the group VIII, IB and IIB [1]. The tolerance of the system to interferences was evaluated by investigating the effect of the ions (a) that are known to be the primary interfering species in the hydride generation reaction and (b) those that can interfere with the retention of selenium on the resin. The following cations were studied: Cu^{2+} , Co^{2+} , Fe^{3+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Zn^{2+} and Mg^{2+} . Additionally, the following anions were studied: HASO_4^{2-} , Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} and ClO_4^- solutions of selenium (0.5 ng ml^{-1}) containing the interfering species in the concentration ranges of 1 – 100 mg l^{-1} (for metal ions and HASO_4^{2-}) and of 100 – 1000 mg l^{-1} (for other anionic species) were prepared. Interference was considered to have occurred when the signal changed by more than $\pm 5\%$ from that for selenium alone (as SeO_3^{2-}). The tolerance limits of the interferences, expressed as the maximum concentrations having no effect, were also determined.

2.4.7. Analytical performance

Standard solutions containing 0 , 100 , 200 , 300 , 400 and 500 ng l^{-1} of Se were used for calibration under the optimal experimental conditions. The percent relative standard deviations (% RSD) of 10 successive measurements of 100 and 200 ng l^{-1} Se solutions were calculated.

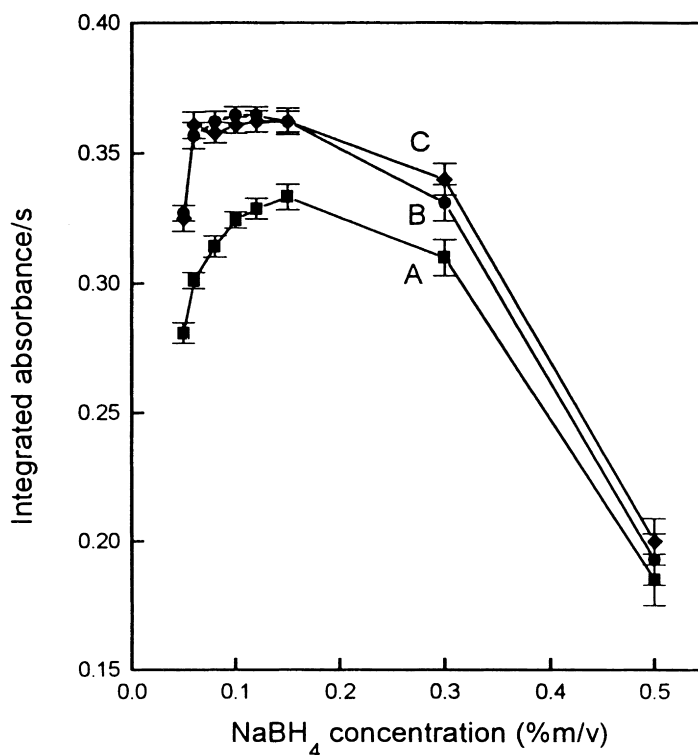


Fig. 2. Effect of the NaBH₄ solution on the peak area (absorbance.s) signal for 500 ng l⁻¹ of Se(IV), for different times that NaBH₄ solution was passed through the column at the flow rate of 5 ml min⁻¹. (A) 30 s; (B) 45 s; (C) 60 s. The error bars are the standard deviations of five replicate measurements.

3. Results and discussion

3.1. Gas-liquid separator

The glass device containing glass beads and the empty plastic vessel (both Perkin-Elmer devices), produced the higher sensitivity (no significant difference between the signal for these devices was found). However, a major carry-over of liquid was obtained with the plastic device. The device constructed in-house from a 25-ml separatory funnel produced a lower signal, though without any carry-over problems. The glass Perkin-Elmer device performed best in terms signal and gas-liquid separation (i.e. less carry-over of liquid) and was used throughout.

3.2. Removal of water vapor and droplets

Both the Nafion dryer and the glass tube prevented the carry-over of moisture to the graphite furnace.

However, it was necessary to clear the moisture from the glass tube from time to time by disconnecting it from the transfer line and flushing with compressed air. The Nafion dryer, which constantly removed the moisture from the transfer line, did not need to be cleaned and was therefore used throughout this work. Although possible analyte losses were not investigated in these studies, results of previous work (on the use of a single-strand Nafion dryer in hydride generation procedures with quartz tube atomization) indicated that while there was evidence for a small loss of arsine, hydrogen selenide was not lost [24].

3.3. Column dimensions and resin type

The results were very similar to those found in the previous work [20]. Consequently, a 150 × 4 mm column packed with Amberlite IRA-410 gel-type resin was used throughout this work.

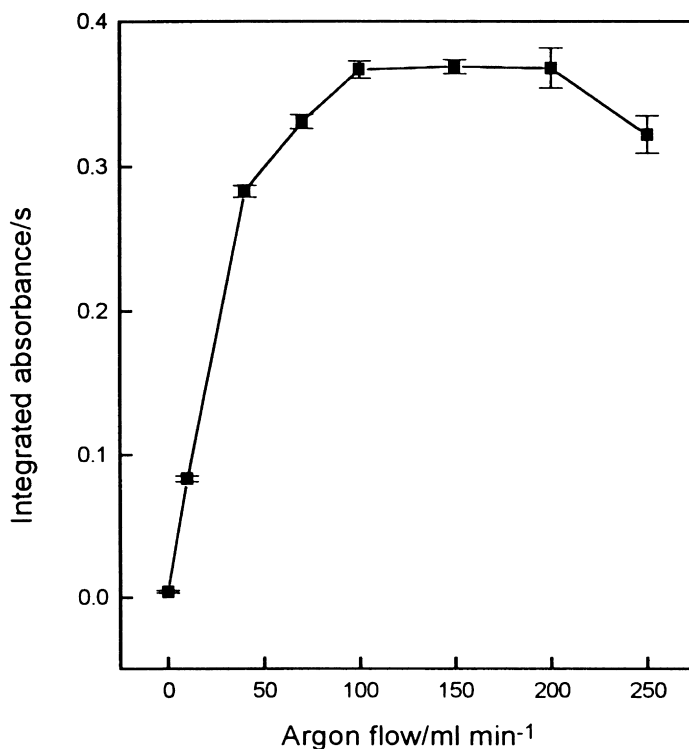


Fig. 3. Effect of the stripping/carrier gas (argon) flow on the net peak area signal for 500 ng l^{-1} of Se(IV). The error bars are the standard deviations for five replicate measurements.

3.4. Parameter optimization

The optimum conditions are given in Table 2. To achieve the best sensitivity, four cycles of the optimization process were necessary. The results of the last cycle for each parameter are presented later. The results for the effect of the borohydride concentration are shown in Fig. 2., from which it can be seen that the maximum signal was obtained in the range 0.10%–0.15% (m/v). Thereafter, the signal decreased as the NaBH_4 concentration increased and, in addition, poorer precision was observed. The signal also depended on the length of time that the reagent was passed through the column, i.e. for the same amount of NaBH_4 (0.15% (m/v) for 30 s, 0.075% (m/v) for 60s), a higher signal was observed for 60 s. This dependence possibly arises as a result of a better distribution of the BH_4^- within the column. The signal increased as the flow rate of the borohydride solution (0.1%) increased from 1.0 to 5 ml min^{-1} . However, for higher flow rates ($5.0\text{--}10 \text{ ml min}^{-1}$), carry-over of

liquid resulting from inefficient gas–liquid separation was observed. A concentration of 0.1% (m/v), a flow rate of 5.0 ml min^{-1} and a time of 60 s, were chosen as optimal for further experiments.

The effect of the carrier gas flow rate is shown in Fig. 3. When no carrier gas was used, no signal was observed, indicating that the hydrogen by-product alone was not sufficient for stripping and transport of the generated hydride to the graphite furnace. When the argon flow was increased from 0 to 100 ml min^{-1} , an increase in the signal was observed. The signal reached a plateau within the range $100\text{--}200 \text{ ml min}^{-1}$. Thereafter, the signal decreased as the flow rate increased, which could be because of inefficient trapping. A flow rate of 150 ml min^{-1} was chosen as optimal.

The effect of the hydrochloric acid concentration on the signal of a pure selenium standard (without interfering species) is shown by trace A in Fig. 4. The signal increased slowly as the HCl concentration increased to 6 mol l^{-1} , then reached a plateau.

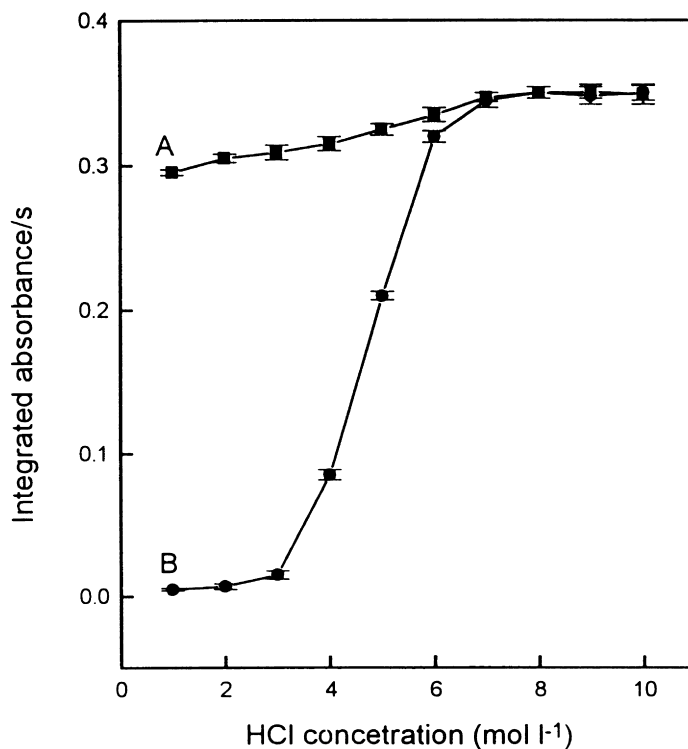


Fig. 4. Effect of the HCl concentration on the peak area (absorbance.s). (A) 500 ng l⁻¹ of Se(IV); (B) 500 ng l⁻¹ of Se(IV) (10 mg l⁻¹ of Cu²⁺). The error bars represent the standard deviation of five replicate measurements.

However, when the analyte was prepared in a solution that contained Cu²⁺, the signal depended very strongly on the acid concentration used for the selenium hydride generation, as shown in trace B in Fig. 4. At low HCl concentrations (less than 4 mol l⁻¹) the signal was totally suppressed. When the acid concentration was increased to 7 mol l⁻¹, a sharp increase in the signal was observed. At high HCl concentrations (greater than 7 mol l⁻¹) the signal was the same as the analyte alone. For the solutions containing copper, a dark precipitate collected on the glass wool at the end of the column when the acid concentration was less than 4 mol l⁻¹.

It is proposed that with the low acid concentrations, borohydride was not completely removed from the column and when the next sample was introduced, the residual borohydride reduced some of the copper matrix to copper metal which then interfered with the subsequent generation of hydrogen selenide. It is well known that borohydride reduces copper and other transition metal ions to their elemental state leading

to the precipitation of these elements [1,25]. Kirkbright and Taddia [26] pointed out that nickel and other Group VIII elements are hydrogenation catalysts and can also adsorb hydrogen in large amounts. Hence, capture and decompositions of the hydride by the finely dispersed metal can occur. Welz and Melcher [25] observed that transition metals begin to affect the determination of selenium only at high interferent concentrations (above 10–100 mg l⁻¹) when present as ions. However, the reaction of gaseous hydrogen selenide with the metallic species, precipitated in a finely dispersed form by the tetrahydroborate, produced a very strong suppression on the signal and so the most obvious means of avoiding this interference would be to prevent reduction and precipitation of the transition metal ions.

In addition, it was observed that for lower acid concentrations, the precipitate did not dissolve completely and thus metal accumulated at the end of the column. Effects similar to that for copper were observed with cobalt, iron and nickel. An HCl

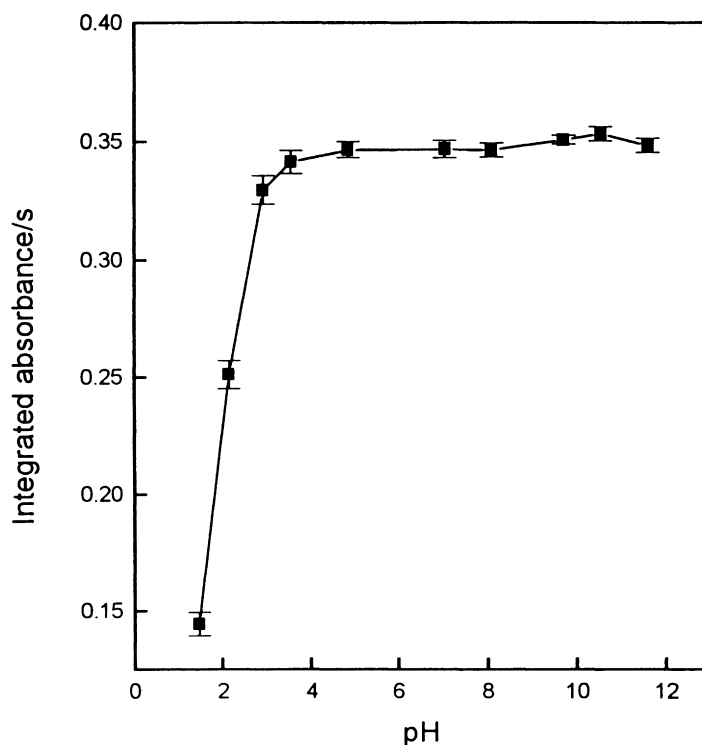


Fig. 5. Effect of the pH of the sample on the peak area signal for 500 ng l^{-1} of Se(IV). The error bars are the standard deviations of five replicate measurements.

concentration of 8 mol l^{-1} was chosen for further experiments.

3.5. Effect of the pH of the sample

The effect of the pH of the sample on the signal is shown in Fig. 5 from which it can be seen that the signal increased as the pH increased up to pH 3. Thereafter, the signal reached a plateau. The effect of pH may be explained by the fact that in an acid medium of pH less than 3, protonation of the selenite produces the neutral compound H_2SeO_3 as the predominant species. At pH 3–6, the mono-negative hydrogenselenite (HSeO_3^-) becomes the predominant species, whereas at pH 6–10 both HSeO_3^- and the selenite ion (SeO_3^{2-}) are present. At pH greater than 10, SeO_3^{2-} predominates. A pH between 7.5 and 8.0 was chosen. At first sight, this pH range might appear sub-optimal as it may lead to the interference of matrix metals which could precipitate as hydroxides (or related species) and be retained by the column.

The value was chosen as the optimum value to be used when titanium(III) chloride and hydrogen peroxide were used for the conversion of selenium to selenium(IV), when the procedure was used as a part of an overall method which incorporated an oxidative sample digestion [27]. As will be discussed later, it was not possible to use hydrochloric acid for this prereduction as the concentration of chloride needed was high enough to prevent accumulation of selenium by the anion-exchange column.

3.6. Effect of interferences

The results for the interference study are shown in Table 5. In the case of the metals, Hg^{2+} was the species which had the largest suppressing effect. The selenium signal was suppressed by 72% when mercury was added in a 200,000-fold mass excess. Iron, as Fe^{3+} , also had a high suppressing effect on the signal. For the rest of the transition metals studied, the tolerance limit (defined as maximum

Table 5
Interferences from diverse elements

Cations ^a	Added as	Relative intensity ^c	Tolerance limit ^d
Cu ²⁺	Cu(NO ₃) ₂	69	50
Co ²⁺	CoCl ₂ 6H ₂ O	100	–
Fe ³⁺	Fe(NO ₃) ₃ 9H ₂ O	40	20
Ni ²⁺	Ni(NO ₃) ₂ 6H ₂ O	81	60
Cd ²⁺	Cd(NO ₃) ₂ 4H ₂ O	86	60
Pb ²⁺	Pb(NO ₃) ₂	78	50
Hg ²⁺	Hg(NO ₃) ₂	28	10
Zn ²⁺	ZnSO ₄ 7H ₂ O	88	70
Mg ²⁺	Mg(NO ₃) ₂ 6H ₂ O	76	50
Anions ^b			
Cl [–]	NaCl	92	900
Br [–]	KBr	100	–
I [–]	KI	95	900
NO ₃ [–]	KNO ₃	82	800
SO ₄ ^{2–}	K ₂ SO ₄	61	500
ClO ₄ [–]	NaClO ₄ H ₂ O	83	800
HAsO ₄ ^{2–a}	Na ₂ HAsO ₄ 7H ₂ O	13	3

^a Added at 200,000 mass excess over selenium.

^b Added at 2,000,000 mass excess over to selenium.

^c Relative to 100 for the peak area signal for selenium (500 ng l^{–1}) alone.

^d Maximum concentration (mg l^{–1}) causing 5% signal depression compared with that for selenium (500 ng l^{–1}) alone.

concentration found to cause a change in signal by less than 5% compared with the signal for selenium alone) was within the range 50–70 mg l^{–1}. As previously discussed, the best way to avoid the interference is to prevent reduction and precipitation of the transition metal ions by the borohydride during the preconcentration step by using high concentrations of HCl (greater than 7 mol l^{–1}). It has been reported that polystyrene-matrix resins have a high affinity for metal chloro complex ions [28,29] and therefore, as the resin is in the chloride form, metals may be retained on the resin during the precon-

centration step. Both iron(III) and Hg(II) form anionic chloro complexes. As the sample pH is slightly alkaline, some metals may be retained on the column as hydroxide species.

The tolerance limit for all the anionic species studied, except for Br[–], was within the range 500–900 mg l^{–1}. No appreciable effect on the signal was observed when Br[–] was added at a 2,000,000-fold mass excess over selenium. Anionic species can compete with selenium for the active sites of the resin and therefore, affect the efficiency of the selenium retention. The highest suppression on the signal

Table 6
Analytical performance of the system

Regression equation	<i>r</i> ^b	LOD (3s) ^c	RSD(%) ^d	
$A = b + mC^a$			100 ng l ^{–1}	200 ng l ^{–1}
$A = 0.0029 + 6.81 \times 10^{-4}C$	0.9997	4 ng l ^{–1}	2.2	1.5

^a A is peak area in absorbance.s, b is intercept, m is slope, C is the concentration of Se in ng l^{–1}.

^b Regression coefficient.

^c LOD (3s) is the detection limit, calculated as 3SD/m. SD is the within-run standard of a blank determination, (n = 10).

^d RSD(%) is the relative standard deviation for 100 and 200 ng l^{–1} of Se, (n = 10).

was produced by As (V) in the form of HASO_4^{2-} . As arsenic is a hydride-forming element, [1] it can compete with selenium for the reductant during the hydride generation step. Therefore, arsenic can suppress the signal by affecting both the retention of the analyte and the generation of H_2Se .

3.7. Analytical performance

The calibration equation and the other performance figures of merit are summarized in Table 6. The system responded linearly from the detection limit up to $2.20 \mu\text{g l}^{-1}$. The precision of the procedure, calculated as the %RSD of 10 determinations of 100 and 200 ng l^{-1} of Se solutions, was 2.25% and 1.46%, respectively. The limit of detection, defined as the concentration giving a signal equal to three times the standard deviation of the blank signal, was 4 ng l^{-1} . The characteristic concentration was 6.46 ng ml^{-1} and thus for a 20-ml sample volume, the characteristic mass was 130 pg. As the characteristic mass for direct introduction of solution in to the furnace is about 45 pg [30] and as the procedures of generation, separation and trapping of hydrogen selenide were determined to be about 75% efficient overall, [16] it may be estimated that the preconcentration and release steps are about 46% efficient.

The detection limit of 60 ng l^{-1} , previously obtained [16] for an FI–HG–ETAAS procedure, which used 1.00 ml of sample, was now decreased to 4 ng l^{-1} for a 20-ml sample volume. As has been discussed in detail elsewhere [31], for FI–HG procedures there is no simple linear relationship between detection limit and sample volume and such an improvement in detection limit could not have been obtained by increasing the sample volume in the ‘conventional’ FI procedure in which the blank signal increases in direct proportion to the sample volume and a situation is rapidly reached in which the detection limit becomes independent of sample volume. The selective retention of the analyte also gives rise to improved tolerance to cationic interferences. For example, it has been previously reported [32] that for the FI determination of selenium the concentration of copper which could be tolerated in the determination of $10 \mu\text{g l}^{-1}$ was about 2 mg l^{-1} whereas, in the procedure reported here, the presence of 50 mg l^{-1} could be tolerated in the determination of

$0.5 \mu\text{g l}^{-1}$. The nature of this interference (retention of the hydrogen selenide on the surface of colloidal metal aggregates) [33] is such that the tolerance limit should be independent of concentration and thus dilution should be effective in removing the suppression. Estimating the detection limit for the FI–HG procedure described by Welz and Schubert-Jacobs to be 200 ng l^{-1} , the ratio of maximum tolerable copper concentration to detection limit is 1×10^4 , whereas for our procedure the ratio is 1×10^7 . On this basis, 10 ng g^{-1} of selenium could be determined in high purity copper.

Acknowledgements

The authors thank the University of the Andes, Merida for financial support for Pablo E. Carrero. The authors also thank Robert I. Ellis for his help and Perkin–Elmer for the provision of the FIAS unit and financial support of Robert I. Ellis.

References

- [1] J. Dedina, D.L. Tsalev, *Hydride Generation Atomic Absorption Spectrometry*, Wiley, Chichester, 1995.
- [2] K.C. Thompson, D.R. Thomerson, Atomic absorption studies on the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin by utilizing the generation of covalent hydrides, *Analyst* 99 (1974) 595–601.
- [3] B. Welz, M. Melcher, Determination of antimony, arsenic, bismuth, selenium, tellurium and tin in metallurgical samples using the hydride AA technique.1: analysis of low-alloy steels, *Spectrochim. Acta Part B* 36B (1981) 439–462.
- [4] D.B. Hatfield, Electrically heated quartz atomization cell for hydride generation atomic-absorption spectrophotometry, *Anal. Chem.* 59 (1987) 1887–1888.
- [5] P.K. Hon, O.W. Lau, S.K. Tsui, Determination of arsenic and antimony by hydride generation atomic-absorption spectrometry using a small hydride generator, *J. Anal. At Spectrom.* 1 (1986) 125–130.
- [6] H. Matusiewicz, R.E. Sturgeon, Atomic spectrometric detection of hydride forming elements following in-situ trapping within a graphite-furnace, *Spectrochim. Acta Part B* 51B (1996) 377–397.
- [7] L. Zhang, S. McIntosh, G.R. Carnrick, W. Slavin, Hydride generation flow-injection using graphite furnace detection, emphasis on determination of tin, *Spectrochim. Acta Part B* 47B (1992) 701–709.
- [8] I.L. Schuttler, M. Feuerstein, G.J. Schlemmer, Long-term stability of a mixed palladium iridium trapping reagent for

- in situ hydride trapping within a graphite electrothermal atomizer, *J. Anal. At. Spectrom.* 7 (1992) 1299–1301.
- [9] G. Tao, Z. Fang, Electrothermal Atomic-absorption spectrometric determination of ultra-trace amounts of tin by in-situ preconcentration in a graphite tube using flow-injection hydride generation with online ion-exchange separation, *Talanta* 42 (1995) 375–383.
- [10] Y. An, S.N. Willie, R.E. Sturgeon, Flow-injection hydride generation determination of arsenic with in situ concentration in a graphite-furnace, *Spectrochim. Acta Part B* 47B (1992) 1403–1410.
- [11] M. Burguera, J.L. Burguera, Flow-injection electrothermal atomic-absorption spectrometry for arsenic speciation using the Fleitmann reaction, *J. Anal. At. Spectrom.* 8 (1993) 229–233.
- [12] M. Walcers, S. Garbos, E. Bulska, A. Hulanicki, Continuous-flow hydride generation for the preconcentration and determination of arsenic and antimony by GFAAS, *Fresenius J. Anal. Chem.* 350 (1994) 662–666.
- [13] C.P. Hanna, G.R. Carrick, S.A. McIntosh, L.C. Guyette, D.E. Bergemann, The determination of selenium in nutritional supplement formulas by flow injection-hydride generation coupled to graphite-furnace atomic-absorption spectrometry, *At. Spectrosc.* 16 (1995) 82–85.
- [14] H.W. Sinemus, H.H. Stabel, B. Radziuk, J. Kleiner, Determination of mercury following sequestration on an iridium coated graphite surface, *Spectrochim. Acta Part B* 48B (1993) 1719–1722.
- [15] D.L. Tsalev, A. D’Ulivo, L. Lampugnani, M. Di Marco, R.J. Zamboni, Thermally stabilized iridium on an integrated, carbide-coated platform as a permanent modifier for hydride-forming elements in electrothermal atomic absorption spectrometry. Part 2. Hydride generation and collection and behaviour of some organoelement species, *J. Anal. At. Spectrom.* 11 (1996) 979–988.
- [16] J.F. Tyson, N.G. Sundin, C.P. Hanna, S.A. McIntosh, Determination of Se in urine by flow-injection hydride generation electrothermal atomic-absorption spectrometry with in-atomizer trapping, *Spectrochim. Acta Part B* 52 (1997) 1773–1781.
- [17] The FIAS-Furnace Technique, Setting Up and Performing Analyses, Publication B3212.10, Part No. B050-9907, Bodenseewerk Perkin-Elmer, Uberlingen, 1993
- [18] S. Tesfalidet, K. Irgum, Polymer-bound tetrahydroborate for arsine generation in a FI system, *Anal. Chem.* 61 (1989) 2079–2082.
- [19] N. Narasaki, Y. Kato, H. Kimura, Semi-automated determination of trace arsenic in river water by HGAAS using tetrahydroborate(III) bound to an anion exchange resin. *Anal. Sci.* 8 (1992) 893–896.
- [20] P.E. Carrero, J.F. Tyson, Determination of selenium by atomic-absorption spectrometry with simultaneous retention of selenium(IV) and tetrahydroborate(III) on an anion-exchange resin followed by flow-injection hydride generation from the solid-phase, *Analyst* 122 (1997) 915–919.
- [21] S. Greenfield, M.S. Salman, M. Thomsen, J.F. Tyson, Comparison of alternating variable search and simplex methods of optimization for inductively coupled plasma optical-emission and atomic fluorescence spectrometry, *J. Anal. At. Spectrom.* 4 (1989) 55–65.
- [22] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, 3rd ed, Ellis Horwood, Chichester, 1993, pp. 185–187
- [23] U. Ornemark, A. Olin, Preconcentration and separation of inorganic selenium on Dowex 1x8 prior to hydride generation-atomic absorption spectrometry, *Talanta* 41 (1994) 67–74.
- [24] N.G. Sundin, J.F. Tyson, C.P. Hanna, S.A. McIntosh, The use of Nafion dryer tubes for moisture removal in flow injection chemical vapor generation atomic absorption spectrometry, *Spectrochim. Acta Part B* 50 (1995) 369–375.
- [25] B. Welz, M. Melcher, Mechanisms of transition-metal interferences in hydride generation atomic-absorption spectrometry Part 1. Influence of cobalt, copper, iron and nickel on selenium determination, *Analyst* 109 (1984) 569–572.
- [26] G.F. Kirkbright, M. Taddia, Application of masking agents in minimizing interferences from some metal ions in the determination of arsenic by atomic absorption spectrometry with the hydride generation technique, *Anal. Chim. Acta* 100 (1978) 145–150.
- [27] P. Carrero, J.F. Tyson, Flow injection determination of selenium by successive retention of Se(IV) and tetrahydroborate(III) on an anion-exchange resin and hydride generation electrothermal atomization atomic absorption spectrometry with in-atomizer trapping. Part 2 Determination of selenium in fresh garlic, *Spectrochim. Acta Part B*, submitted
- [28] K. Brajter, K. Slonawska, Matrix separation of palladium and iridium by the cellulose anion-exchanger Cellex-t and the subsequent determination of palladium at the ($\mu\text{g/g}$ -level), *Mikrochim. Acta I* (1989) 137–143.
- [29] K. Brajter, K. Slonawska, Gold trace separation from some platinum group-metals on cationic exchanger in the presence of amines, *Anal. Lett.* 21 (1988) 311–318.
- [30] Recommended Conditions for THGA Furnaces, Publication number B3110.06, Perkin-Elmer, Uberlingen, 1991
- [31] J.F. Tyson, R.I. Ellis, S.A. McIntosh, C.P. Hanna, Effect of sample volume on the limit of detection in flow injection hydride generation electrothermal atomic absorption spectrometry, *J. Anal. At. Spectrom.* 13 (1998) 17–21.
- [32] B. Welz, M. Schubert-Jacobs, Evaluation of a flow injection system and optimization of parameters for hydride generation atomic absorption spectrometry, *atomic spectrosc.* 12 (1991) 91–104.
- [33] A. D’Ulivo, L. Lampugnani, R. Zamboni, Interference of copper, silver and gold in the determination of selenium by hydride generation atomic fluorescence spectrometry: an approach to the studies of transition metal interferences, *J. Anal. At. Spectrom.* 6 (1991) 566–571.