A metallic furnace atomizer in hydride generation atomic absorption spectrometry: Determination of bismuth and selenium[☆]

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ABSTRACT

A flow injection hydride generation system with a metal furnace atomizer (Inconel 600® alloy) was employed for Bi and Se determination. The presented methods have linear ranges up to 200 and 500 μg L^{-1} for Bi and Se, respectively, with good linearities (r^2=0.9997 and 0.9974, respectively). The limits of quantification obtained according to IUPAC recommendations were 2.3 μg L^{-1} for Bi and 6 μg L^{-1} for Se, and the relative standard deviations (N=6) based on Bi and Se analytical responses from real samples were 2.7% and 10%, respectively. Accuracy evaluations were based on certified materials such as SRM 361, SRM 363, and SRM 364 (steel alloys) for Bi, Mess-3 (marine sediment), SRM 397 (human hair), and Bio-Rad2 — 69042 (urine) for Se. Good agreements between the results were obtained at the 95% confidence level, according to the t-test.

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1. Introduction

An important aim of analytical chemistry is to improve the selectivity and sensitivity of analytical methods, which can often be accomplished by working with specific selective techniques that have good high sensitivity (i.e. electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma mass spectrometry (ICP-MS), neutron activation analysis (NAA)). Alternatively, the use of a separation or concentration steps in the analytical procedure (i.e., resin columns [1], imprinted polymers [2], solid phase extraction/ microextraction [3]) can be employed.

Hydride generation atomic absorption spectrometry (HGAAS) is a good alternative in terms of analytical technique since the analyte is released from the matrix due to formation of a volatile hydride, and several matrix interferences can be overcome through the hydride generation process [4–6]. However, specificity and selectivity are often difficult to attain due to the relatively high number of concomitants that can produce and transport volatile species to a given detector. Thus, the coupling of an efficient hydride generation system to atomic absorption spectrometry should allow both specificity and the power of detection to be combined and improved [7]. When on-line hydride generation is carried out, specific limitations related to the poor linearity and low resistance to atomization interferences are observed when a quartz tube atomizer (QTA) is employed. Although such drawbacks can be circumvented by using a heated quartz tube atomizer (HQTA) [8] or a multiple microflame quartz tube atomizer (MMQTA) [6], the QTA remains the most popular approach for hydride generation applications.

Recently, Figueiredo et al. [9] reported an alternative to hydride atomizers based upon a flame-heated metal furnace. These authors highlighted certain advantages of this system, such as good sensitivity, selectivity, linear range, precision, and accuracy when applied to the determination of Sb content through hydride generation using a metal furnace as atomizer. In the context of the potential application of these metal furnace atomizers to hydride generation, we herein describe the extension of this system to Bi and Se determinations in medicine, urine, and certified reference samples.

2. Experimental

2.1. Apparatus

A Perkin–Elmer AAnalyst 300 flame atomic absorption spectrometer equipped with deuterium lamp background correction and PE-AA WinLab software was used for all Se and Bi determinations. Electrodeless discharge lamps (EDL) were used as primary radiation sources, and operating conditions were those recommended by the manufacturer (λ=196.0 nm and 0.7 nm spectral band pass for Se; λ=223.1 nm and

0.2 nm spectral band pass for Bi). All measurements were based on integrated absorbances.

The on-line hydride generation system consisted of an Ismatec peristaltic pump (IPC-12, Glattzbrugg, Switzerland) and a polymethacrylate three-piece injector-commuter device [10] designed and constructed in our laboratories. Polyethylene tubes (0.7 mm i.d.) were used as transmission lines, and Tygon® tubes were used for propelling the solutions. A Provecto Analítica microwave oven, model DGT Plus (Jundiaí, Brazil), was used for sample decomposition. High purity deionized water (18.2 MΩ cm) was obtained from a Millipore model Milli-Q Plus water purification unit.

2.2. Reagents and solutions

All solutions were prepared using analytical or reagent grade salts and deionized water. All glassware was washed with soap and kept in 10% (v/v) HCl for 24 h with posterior cleaning with ultra-pure water. Reference solutions of Se or Bi were prepared daily using 7.0 or 0.3 mol L^{-1} HCl, respectively, by serial dilution from standard stock solutions containing 1000 mg L^{-1} (Tec-Lab, Jundiaí, São Paulo, Brazil) in deionized water. 0.5% and 1% (w/v) $NaBH_4$ (Aldrich, Steinheim, Germany) solutions were also prepared daily in 1% and 0.5% (w/v) NaOH (Merck, Darmstadt, Germany) for Se and Bi determinations, respectively.

2.3. Samples

Two medicinal samples (Peptosil and Bisuisan) were purchased from local pharmacies. SRM 361, SRM 363, and SRM 364 (steel alloys) reference materials were obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), and were used for Bi determination. For Se determination, three certified materials were employed. These included: SRM 397 (human hair) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), Mess-3 (marine sediment) from the National Research Council Canada, and Bio-Rad2 — 69042 (urine) from Bio-Rad Laboratories GMbH, Munich, Germany.

2.4. Sample preparation

2.4.1. Bi determination

Steel alloy: A 500-mg sample was dissolved in 20 mL aqua regia with gentle heating (70 °C), and the volume was reduced to near dryness. After filtration, the solution was transferred to a 25-mL volumetric flask in 1.0 mol L^{-1} HCl.

Peptosil (Bi subsalicilate): A 100-mg sample was dissolved in 10 mL 5.0 mol L^{-1} HCl, and heated at 70 °C until near dryness. The final solution was quantitatively transferred to a 100-mL volumetric flask. Next, 16 μL of this solution was transferred to a 25 mL volumetric flask, and the final volume was adjusted using 0.3 mol L^{-1} HCl.

Bisuisan (basic Bi carbonate): A 100-mg sample was placed in a Teflon flask, and 2 mL conc. HNO_3 (14.3 mol L^{-1}) and 1 mL 30% (v/v) H_2O_2 were added. A 40-min pre-digestion was carried out, and microwave-assisted sample decomposition was performed according to the following sequence: 5 min at 200 W, 5 min at 400 W, and 5 min at 790 W. Next, the sample was heated (at 70 °C) to near dryness, transferred to a 250-mL volumetric flask, and the final volume was adjusted with 0.3 mol L^{-1} HCl. Finally, this solution was diluted 200 times to obtain the reference solution for all Bi determination.

2.4.2. Se determination

Marine sediment (Mess-3) and human hair (SRM 397): For both samples, a 300-mg mass was placed in a Teflon flask. Next, 5 mL aqua regia and 2 mL 27.6 mol L^{-1} hydrofluoric acid were added to the Mess-3 sample, while 4.2 mL of 14.3 mol L^{-1} HNO_3 were added to the SRM

397 sample. For both samples, 1 mL 10% (m/v) sulfamic acid (Carlo Erba, Milan, Italy) was added for NO_x elimination [11], and a 60-min pre-digestion was carried out. The microwave-assisted digestion for marine sediment was then performed according to the following sequence: 3 min at 200 W, 5 min at 400 W, 5 min at 600 W, and 20 min at 700 W. 200 mg boric acid was added for fluoride volatilization. The microwave-assisted digestion for human hair sample was carried out according to the following 5-step sequence: 5 min at 200 W, 5 min at 300 W, 5 min at 400 W, 5 min at 600 W, and 2 min at 800 W. After microwave sample decomposition, the samples were heated to near dryness. At this point, a filtration step was required for all Mess-3 samples. For marine sediment and human hair samples, 2 mL and 1.6 mL, respectively, were transferred to 10-mL volumetric flasks, and the final volumes were adjusted with 7 mol L^{-1} HCl.

Urine (Bio-Rad2 — 9042): For digestion, 1.45 mL of the urine sample and the same volume of 14.3 mol L^{-1} HNO_3 were transferred to a beaker, and the samples were heated to near dryness. Next, 0.8 mL of 12.0 mol L^{-1} HCl was added, and the samples were again heated to near dryness, and then transferred to a 10-mL volumetric flask with 7 mol L^{-1} HCl [12].

Se hydride generation requires that all analyte be Se(IV). As such, mineralized samples were transferred to a polyethylene flask, and heated to 90 °C for 15 min in order to guarantee complete reduction of Se(VI) to Se(IV) [13]. The solution was stored at room temperature.

2.5. Flow system

The Se and Bi hydrides were prepared by the reaction of Se(IV) or Bi(III) with $NaBH_4$ in an acidic medium. 7.0 mol L^{-1} HCl was employed for Se, and 0.3 mol L^{-1} HCl was employed for Bi. The generated hydrides were introduced into a gas–liquid separator [14], where each was transported by a constant argon flow towards the atomizer (Inconel600® tube atomizer — Camacam, São Paulo, Brazil). The atomizer was fixed on the burner of the flame atomic absorption spectrometer using a lab-made steel support with four ceramic pins, with atomizer dimensions similar to those commonly used in thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) [15]. The tube also contained six holes in the face on the burner
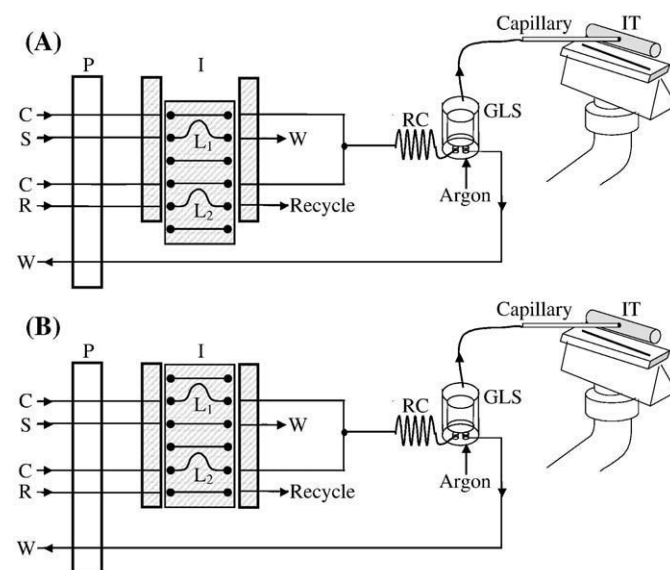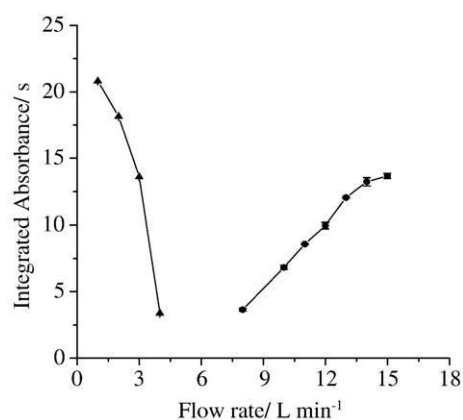

Fig. 1. Schematic diagram of the flow injection system proposed. [P]: peristaltic pump; [I]: injector–commuter; [x]: confluence point; [RC]: reaction coil; [GLS]: gas–liquid separator; ceramic capillary and INCONEL600® tube (IT); [C] carrier solution (deionized water); [S] standards/samples (in acidic media); [R] $NaBH_4$ in NaOH; [W] waste. (A) System in the sampling position. [L₁]: Sample; [L₂]: $NaBH_4$ in NaOH. (B) System in injection position.

(A)

(B)

(C)
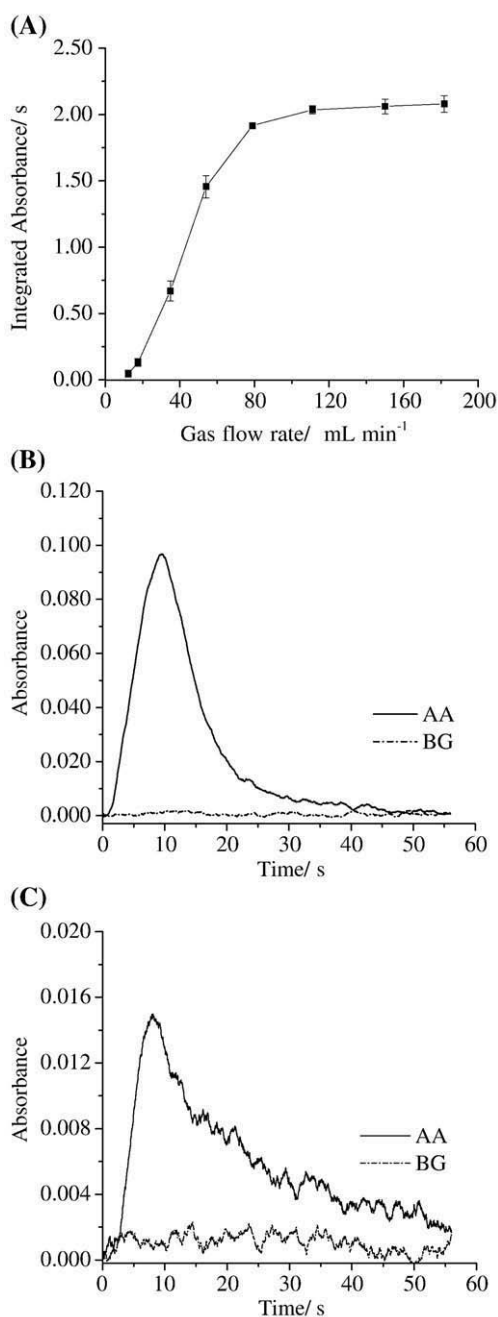
Fig. 2. (A) Effect of Ar carrier flow rate on the efficiency of bismuthine generation; (B) Analytical profile, 150 mL min^{-1} flow rate; (C) Analytical profile, 35 mL min^{-1} flow rate. AA: atomic absorption. BG: background. Error bars indicate sample standard deviations (s) from the results obtained (N=3) for each tested value.

Fig. 3. Optimization of the acetylene:air ratio. ▲ Integrated absorbance values for different air flow rates with the acetylene flow rate fixed at 3 L min^{-1}. ● Integrated absorbance values for different acetylene flow rates with the air flow rate fixed at 15 L min^{-1}. Experimental conditions: 400 μg L^{-1} Se solution, 7 mol L^{-1} HCl, 1% (m/v) NaBH$_4$, 0.1% (m/v) NaOH.

hydride generation, a gas–liquid separator (GLS) was employed, and the hydrides were transported to the upper part of the system by a constant argon flow at 68.2 mL min^{-1} for Se hydride and 150 mL min^{-1} for bismuthine. The remaining sample was aspirated through a lateral hole in the GLS and discarded. Finally, the hydrides were passed through the ceramic capillary (1.5 mm i.d., 2.0 mm o.d. and

(A)

(B)

Fig. 4. Influence of the drilled hole area on the bismuth (A) and selenium (B) analytical responses using an atomizer without holes and with 19, 43, 67, 91, and 115 mm^2 of total hole area. Error bars indicate sample standard deviations (s) from the results obtained (N=3) for each tested value.
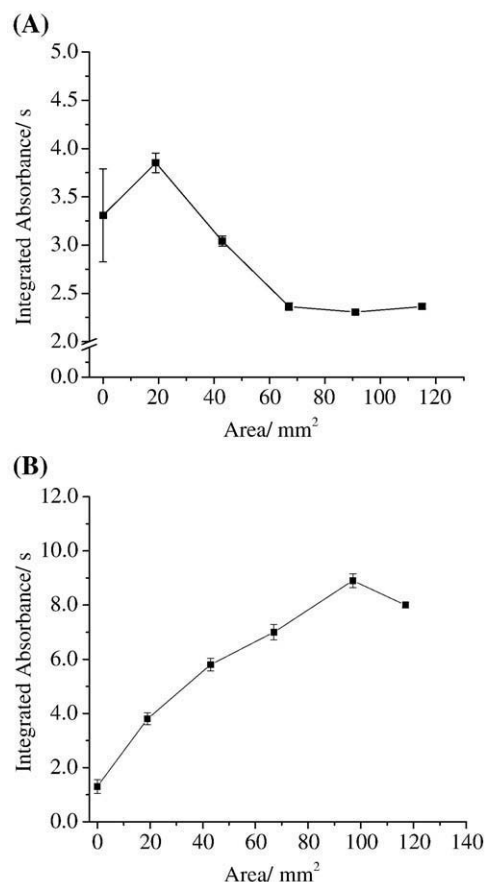
side, allowing for partial flame penetration inside the tube. It also contained a lateral hole where a ceramic tube, employed for sample introduction, was inserted up to ca. 2 mm. The tube atomizer composition (>72% (m/m) Ni, 14–17% (m/m) Cr and 6–10% (m/m) Fe) was obtained from the manufacturer (Camacam, São Paulo, Brazil).

Fig. 1 illustrates the flow system. In the sampling position (Fig. 1A), the L$_1$ (samples) and L$_2$ (NaBH$_4$) loops were filled with 1600 μL of the respective samples. When the central portion of the injector was switched to the alternative position (Fig. 1B), the C$_1$ and C$_2$ carrier streams (deionized water) transported the volumes in the L$_1$ and L$_2$ loops toward the analytical pathway. Next, the acidified sample (Se(IV) or Bi(III)) and the reducing agent (BH$_4^-$) were mixed at the 'x' confluence point, generating the requisite hydride. After

Table 1

Analytical parameters obtained for Bi and Se determination

Parameters	Bi	Se
Regression equation	$Y = 0.03353 + 0.08981X$	$Y = -0.2282 + 0.058X$
R^2	0.9997	0.9974
LOD (μg L^{-1})	0.7	1.8
Limit of quantification — LOQ (μg L^{-1})	2.3	6
Linear range (μg L^{-1})	2.3–200	6–500
Precision (%)[a]	<2.7	<10

[a] Based on Bi and Se analytical responses from samples (as repeatability), $N = 6$.

100 mm length) to the heated Inconel600® atomizer tube [9], where Se or Bi were determined.

3. Results and discussion

3.1. Optimization of the variables for Bi(III) and Se(IV) determination

All optimizations were carried out using an Inconel600® tube atomizer [9], with 50 μg L^{-1} for Bi reference solutions and 400 μg L^{-1} Se reference solutions.

3.1.1. Effects of reagent concentrations and flow parameters

Since HCl is recommended for hydride generation [8], varying concentrations ranging from 0.12 to 1.92 mol L^{-1} were tested to obtain the optimal efficiency in terms of bismuthine generation. Only slight vriations (ca. 2%) in the results were observed with HCl concentrations greater than 0.3 mol L^{-1}. This mineral acid was also used for Se hydride generation [16], and a concentration of 7.0 mol L^{-1} was chosen for this work.

The effects of sodium borohydride concentrations in the range between 0.02 and 1.5% (m/v) for Bi and in the range between 0.1 and 2% (m/v) for Se were also tested. The optimal analytical results were obtained at 1% (m/v) and 0.5% (m/v) for Bi and Se, respectively.

Sampling loop volume ranges from 300 to 2000 μL were tested and the carrier flow rate was examined between 6.0 and 13.4 mL min^{-1} for both Bi and Se determinations. A volume of 1600 μL and a flow rate of 11.3 mL min^{-1} (integrated absorbance of ca. 1.5) were chosen for Bi, while 600 μL and 10.0 mL min^{-1} were chosen for Se determination. These values were selected as compromises among sample quantity, sample throughput, and peak shape quality.

After defining the injection volume and carrier flow rate, reactor coil lengths (10–90 cm range) were evaluated. The optimal conditions

Table 2

Comparison of the LOD attained with the proposed work and others techniques reported in the literature

Techniques	Se LOD (μg L^{-1})	Bi LOD (μg L^{-1})	Reference
HG-MF-AAS[a]	1.8	0.7	
FI-HGAAS[b] (pre-concentration) (3σ)	–	0.225	[5]
QTAW[c] system coupled to FI-HGAAS	–	3.8	[14]
ETAAS (3σ)	3.7	–	[19]
HPLC-HGAAS[d]	2.4	–	[20]
HGAAS	10.6	–	[21]
LC-UV-HGAFS[e]	0.5	–	[22]
HS-SDME-ETAAS[f] (pre-concentration) (3σ)	0.15	–	[23]
ETAAS	5	–	[24]
ETAAS	–	2.9	[25]
HGAAS	–	0.30–0.84	[26]

[a] Hydride generation metal furnace atomic absorption spectrometry.
[b] Flow injection hydride generation atomic absorption spectrometry.
[c] Quartz tube atomizer with tungsten coil.
[d] High performance liquid chromatography hydride generation atomic absorption spectrometry.
[e] Liquid chromatography UV irradiation hydride generation atomic fluorescence spectrometry.
[f] Headspace single-drop microextraction electrothermal atomic absorption spectrometry.

Table 3

Bi determination in different samples using the proposed method and two other techniques (ETAAS or FAAS)

Sample	Proposed method	ETAAS	FAAS	Reference value
Bismuth basic carbonate (mg g^{-1})[a]	29.9±0.3	28±2	–	–
Bismuth subsalicilate (mg g^{-1})[a]	152±7	–	144±2	–
[b]SRM 361 (%, w/w)	$(37\pm1).10^{-5}$	–	–	0.0004
[b]SRM 363 (%, w/w)	$(6\pm1.4).10^{-5}$	–	–	0.0008
[b]SRM 364 (%, w/w)	$(13\pm7).10^{-5}$	–	–	0.0009

[a] $x \pm t.~\sigma/(n)^{1/2}$, $N = 3$.
[b] $x \pm$ SD, $N = 4$, (steel alloy).

employed a reaction coil length of 30 cm, with a 1600 μL injection volume. Under these conditions, the highest analytical signal (3.0 s) with good repeatability (RSD ca. 1%) was obtained. This coil length value was employed for both Se and Bi determinations.

3.1.2. Effect of argon gas flow rate

The argon flow rate has a significant effect on Bi detectability (Fig. 2A), since bismuthine must be rapidly transported to the atomizer due to instability [8]. This is confirmed by comparing Fig. 2B and C. In Fig. 2C, more effective Bi atomization is obtained at higher argon flow rates; at a 150 mL min^{-1} flow rate, the integrated absorbance increases by up to 1.97. Additionally, as shown in Fig. 2B, a better peak shape was obtained compared to that presented in Fig. 2C, where a noisy tail is evident. Due to these observations, a 150 mL min^{-1} argon flow rate was chosen for further experiments.

Contrary to the bismuthine results, no argon flow rate effect was observed on the Se analytical signal within 45.1 and 165 mL min^{-1} range. Only slight variations (up to 8%) were observed in the integrated absorbance. As such, an argon flow rate of 68.2 mL min^{-1} was chosen, as a compromise between analytical frequency and Se peak shape.

3.1.3. Effect of the acetylene and air flow rates

The acetylene and air flow rates were evaluated in the 1 to 4 L min^{-1} and 8 to 12 L min^{-1} ranges for Bi determination. Measurement were consistently made in a univariate way. For Bi determinations, an increase of 30% in the analytical signal was observed when comparing the 4 and 10 L min^{-1} with 3 and 8 L min^{-1} flow rates for acetylene and air, respectively. However, under the first of these conditions, the transient analytical profiles presented an intense drift, a delay in returning to the baseline, and higher background signals. Thus, a 3 L min^{-1} acetylene flow rate, and a 10 L min^{-1} air flow rate were chosen for further experiments. According to Fig. 3, the optimal result for Se determination was obtained using 1 and 15 L min^{-1} flow rates for acetylene and air, respectively.

3.1.4. Effect of ceramic capillary inner diameter

Three different inner diameters (0.5, 1.0, and 1.5 mm) were evaluated, and the optimal results were obtained with 1.5 mm i.d. for both Bi and Se. This condition was used for all subsequent work.

3.1.5. Effect of the Inconel600® tube hole area

Various metallic atomizer total hole areas (19, 43, 67, 91, and 117 mm^2) were studied. Atomizers without holes were also evaluated.

Table 4

Se determination in different samples

Sample	Proposed method (mg kg^{-1})[a]	Acceptable range (μg L^{-1})	Certified value (mg kg^{-1})
SRM 397 (human hair)	1.9±0.5	–	2.00±0.08
Mess-3 (marine sediment)	0.67±0.12	–	0.72±0.05
Bio-Rad2 — 69042 (urine)	168±26	165–249	–

[a] $x \pm t.\sigma/(n)^{1/2}$, $N = 3$.

As shown in Fig. 4A, the best analytical signal was obtained with a 19 mm^2 total hole area. At values greater than 43 mm^2, the integrated absorbance decreases. As such, 19 mm^2 as the total atomizer hole area was deemed optimal for bismuthine atomization, and employed for further experiments.

For Se, however, the best analytical result was obtained with 91 mm^2 as the total atomizer hole area (Fig. 4B), and used for all further experiments. These results are in agreement with those obtained when flame composition was evaluated.

3.2. Interferences

Interferences in hydride generation can be classified as either liquid phase interferences, transport interferences, or atomizer interferences [8]. As the interferences directly related to dissolved inorganic compounds are most frequently studied [8], certain elements were concomitantly evaluated in the Bi and Se determinations. Interference effects were considered when recoveries of Bi and Se were greater than 110% or below 90%. Four elements (Ag, Cu, Fe and Ni) were considered as potential concomitants in the Bi determination. Interferences ranging from 15.0% to 72.8% were detected from 1:10 Bi:concomitant proportions when testing Ag, Cu, and Fe. A reduction of 35% in the Bi absorbance signal was observed when a 1:1 Bi:Ni proportion was tested.

Interferences in the determination of Se content, in the presence of As, Bi, and Cu were observed from 1:10, 1:100, and 1:50 Se:concomitant proportions, respectively. With these proportions, the Se recoveries were 73%, 49%, and 65% when As, Bi and Cu, respectively, were tested as concomitants.

3.3. Figures of merit

The figures of merit for Bi and Se determinations are presented in Table 1. The limits of detection (LOD) obtained are comparable to or better than those reported in the literature (see Table 2). These references were chosen for comparing the performance of our proposal with existing techniques. More information related to similar methods based on externally heated quartz tube atomizers have been reported [17].

3.4. Method validation

The accuracy of the methods for Bi and Se determination were verified with antacid and steel samples, and six different certified materials. The results are presented in Tables 3 and 4, and show that the obtained values are in agreement at a 95% confidence level (according to the *t*-test) with the certified samples (steel, urine, human hair, marine sediment) as well as with those obtained by alternative techniques (antacid samples).

Although some interferences for Bi and Se were noted, as discussed (see item 3.2), a masking agent was not needed to overcome Bi interferences because Fe(III), present in the steel alloy samples, sufficiently masks interferences caused by other transition metals (Table 3) [18]. For Se determination, these interferences were not detected since the analyzed samples were either free of the concomitants or had their concentrations below the proportions tested in item 3.2 (Table 4).

4. Conclusions

The use of a metal furnace as an atomizer in hydride generation was successfully extended to Bi and Se determinations in specific complex samples, as initially proposed. These methods presented figures of merit comparable to or better than examples from the literature (Table 2). Moreover, the good LOD attained for the analytes, the linear range, and the accuracy underscores the potential applicability of the proposed methods employing metallic atomizers.

Due to the inherent chemical and physical resistances of the system, more than 2000 determinations for Bi and more than 4000 determinations for Se were carried out in this work with no substantial changes in the furnace structure, highlighting the extended atomizer lifetime and durability.

Finally, the low cost (ca. US $7/tube) and good analytical performances obtained for both Bi and Se suggest that the metallic atomizers should be considered as powerful alternatives for hydride generation techniques in commercial and laboratory settings.

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