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Simultaneous determination of As, Bi, Sb, Se, Sn and Te in lead alloy using flow injection-hydride generation-inductively coupled plasma mass spectrometry

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A method based on flow injection-hydride generation-inductively coupled plasma mass spectrometry (FI-HG-ICP-MS) for the determination of trace amounts of As, Bi, Sb, Se, Sn and Te in lead alloys was developed. The analytical parameters for the analyte determination were 0.60% m/v sodium tetrahydroborate (2.6 mL min^{-1}); 90 μL sample volume and 1.25 L min^{-1} carrier gas (Ar) flow rate. Hydrochloric acid (6.0 mol L^{-1} for As, Bi, Se and Te and 0.1 mol L^{-1} for Sb and Sn) was used as sample carrier at 7.4 mL min^{-1}. Three FI systems were developed and consist of a single channel and dual channel, with one and two gas–liquid separators, respectively. The systems with a dual channel permit the simultaneous determination of all elements, by using two reaction conditions. The effect of Ag, Bi, Cu, Pb, Sb and Te, which were the main elements present in the sample, on the analyte determination was evaluated. With the use of optimized experimental conditions, all elements could be determined by external calibration. The LOQ were 0.14, 0.02, 0.03, 0.02, 0.02 and 0.02 μg g^{-1} for As, Bi, Sb, Se, Sn and Te, respectively, and the RSD was 8% or lower for five consecutive measurements of a sample solution. Analyte recoveries were in the range of 94 to 101% and the results were in good agreement with those obtained by ICP OES. The method was applied to determine the analytes in lead alloy samples used in automotive battery manufacture, with a sample throughput of 10 determinations h^{-1}.

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1. Introduction

Lead and lead alloys are widely used as bullets, special aprons, cable sheathing, solders, battery grids, pipes, castings, in the chemical industry and for other applications. As pure lead is very soft and ductile, many applications use it in the form of an alloy. Alloys formed with tin, copper, arsenic, aluminium, antimony, bismuth, cadmium, silver, tellurium, calcium and sodium are of industrial importance.[1] These elements are added to give unique characteristics to the final product, mainly for increasing hardness and strength. In this sense, anodes made of lead containing Ag, Co or Tl are most resistant to corrosion compared with pure lead when used in the electrorecovery and plating of metals such as Mn, Cu, Ni and Zn.[2] Rolled Pb–Ca–Sn and Pb–Ag alloys are the preferred anode materials in these applications because of their high resistance to corrosion by the sulphuric acid used in electrolytic solutions. Lead anodes also have high resistance to corrosion by seawater, making them economical to use in systems for cathodic protection of ships and offshore oil platforms. In the case of automotive batteries, controlled quantities of Ag, As, Ca, Cu, Sb, Se, Te and Sn are added in order to increase hardness, provide resistance to corrosion, control grain size, minimize problems with fissures, avoid electrolyte decomposition, and impart other characteristics.[3–7] Therefore, depending upon the particular uses of lead and lead alloys, it is necessary to rigorously control these elements in the final product. However, severe interference may occur in the determination of minor elements, especially those present in concentrations in the range of μg g^{-1} (trace elements) or lower (ultra-trace), mainly due to the high concentration of Pb. Direct determination of the composition of metals and metal alloys can be done by spark optical emission spectrometry,[8] glow discharge optical emission spectrometry,[9] and X-ray atomic fluorescence,[10] among others. In general, for these techniques it is not necessary to decompose the sample, consequently reducing the analysis time and reducing the generation of laboratory residues. However, sometimes the limit of detection (LOD) is not sufficiently low to detect the elements. On the other hand, inductively coupled plasma optical emission spectrometry (ICP OES) and mass spectrometry (ICP-MS), atomic fluorescence spectrometry (AFS) and atomic absorption spectrometry (AAS) are widely employed for elemental determination in different types of samples. Among these techniques, ICP-MS and ICP OES have an important role, mainly because of their multi-element analysis capability,

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though the LOD of ICP OES may not be low enough for the determination of impurities in high-purity metals and metal alloys. In this respect, the ICP-MS technique would be more appropriate. However, the use of this technique for the analysis of metals and metal alloys is prone to spectral and non-spectral interferences, especially the space-charge effect and deposition of materials on the interface.[11,12] In general, the interferences can be overcome by matrix separation using solid phase extraction, liquid–liquid extraction or by using the hydride generation (HG) technique. In particular, the HG technique improves the LOD and allows the separation of the analytes from the sample matrix before measurement.[13] With the use of HG coupled to ICP-MS it is possible to determine low concentrations of volatile hydride-forming elements and to minimize interference problems. However, interferences caused by some transition metals as well as between the volatile hydride-forming elements have been documented.[13–15] To overcome these kinds of interferences, procedures such as the use of masking agents,[16–19] higher acid concentrations for the reaction,[13] and reactions carried out in flow systems have been proposed.[20–23]

In addition, to circumvent some problems of interference in HG, the continuous flow (CF) and, in particular, flow injection (FI) systems are important devices that facilitate sample handling, minimize problems of sample contamination, allow working with smaller sample and reagent quantities and make the analysis faster.[24,25] Moreover, when FI systems are used for hydride generation, spectral and non-spectral interferences are minimized in the ICP-MS technique and the LOD is improved. In this way, elements such as As, Ge and Te have been determined in nickel-based alloys.[23,26] However, in both studies, the authors used masking agents and a dynamic reaction cell (DRC) to minimize interferences. Even so, it was necessary to determine the elements by standard addition and/or isotope dilution.

Considering the characteristics of the flow injection-hydride generation technique and the high sensitivity and multi-elemental capability of ICP-MS, the coupling of these techniques could be suitable to determine low concentrations of volatile hydride-forming elements. In this context, in the work reported here we investigate different FI configurations for the determination by ICP-MS of As, Bi, Sb, Se, Sn and Te in lead alloys used for battery manufacture. Chemical and physical parameters of FI-HG systems were evaluated in order to determine the analytes in the samples.

2. Materials and methods

2.1. Instrumentation

An inductively coupled plasma mass spectrometer (PerkinElmer SCIEX, model ELAN DRC II, Canada) was used for As, Bi, Sb, Se, Sn and Te determination. All measurements were processed in integrated signal (peak area). The elements were determined using $^{75}As^+$, $^{209}Bi^+$, $^{121}Sb^+$, $^{82}Se^+$, $^{119}Sn^+$ and $^{130}Te^+$ isotopes. Highest abundance and freedom from interference were the criteria used in selecting these isotopes. The spectrometer was adjusted in order to obtain the highest sensitivity (highest signal-to-background ratio – SBR) for all analytes by using the flow injection-hydride generation system.

The FI systems consist of an eight channel peristaltic pump (Gilson, Minipuls 3-France), an injection valve and a "U" (l = 100 mm; i.d. = 1.5 mm) type gas/liquid (G/L) separator. The overall system is interconnected by polytetrafluorethylene (PTFE) tubing (i.d. = 0.8 mm) and a PTFE (i.d. = 4.0 mm) tube is used to connect the G/L separator to the ICP torch. Tygon tubes were used for the peristaltic pump. The FI-HG-ICP-MS manifolds are shown in Fig. 1.

2.2. Reagents and solutions

All chemicals were of analytical reagent grade. Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q purifier system (Millipore Corp., USA). Hydrochloric acid and HNO_3 were purified by sub-boiling distillation in a quartz still (Milestone Duopur, Italy). Argon of 99.996% purity (White Martins, Brazil) was used for plasma generation and as a carrier gas. Mono-elemental and multi-elemental working solutions of As(III), As(V), Bi(III), Sb(III), Sb(V), Se(IV), Sn(II), Sn(IV), and Te(IV) were prepared from serial dilutions of 1000 mg L^{-1} (Merck, Germany) stock solutions.

Calibration curves in the range of 1.0 to 15.0 μg L^{-1} were prepared in HCl or in ultrapure water in accordance with the test for hydride generation (see Section 3.4). Sodium tetrahydroborate ($NaBH_4$, Nuclear, Brazil) solution was prepared by dissolving the solid reagent in 0.05% (m/v) NaOH solution (Vetec, Brazil). Lead (1000 mg L^{-1}) and Ag (1000 mg L^{-1}) were prepared from lead nitrate ($Pb(NO_3)_2$, Merck) and silver nitrate ($AgNO_3$, Vetec) by dissolving the salts in 2% (v/v) purified nitric acid. A 1000 mg L^{-1} Cu (Spex, USA) solution (5% v/v HNO_3) was also used.

2.3. Samples and sample preparation

Lead alloys employed in automotive batteries were analysed. Bulk samples were transformed into small pieces. Sample amounts of 1000 mg were solubilised in a 200 mL beaker using 12 mL of concentrated nitric acid and 3 mL of concentrated hydrochloric acid. The sample and the mixture were gently boiled on a heating plate until complete sample dissolution occurred. Finally, the sample solution was evaporated to near dryness in order to obtain a white precipitate. The precipitate was dissolved in water and the volume made up to 50 mL in a volumetric flask. Appropriate dilutions were performed to analyse the sample solutions by FI-HG-ICP-MS.

2.4. Method development

Solution flow rates (sample carrier and $NaBH_4$), reagent concentrations (HCl and $NaBH_4$), sample volume and reactor length (R_1 and R_2) of the FI systems were adjusted in order to obtain the highest sensitivity.

The influence of the main components of the sample (for instance, Ag, Bi, Cu, Pb, Sb and Te) on analyte determination was evaluated. The effect of the HCl concentration of the sample and carrier solutions, and sample volume was evaluated in

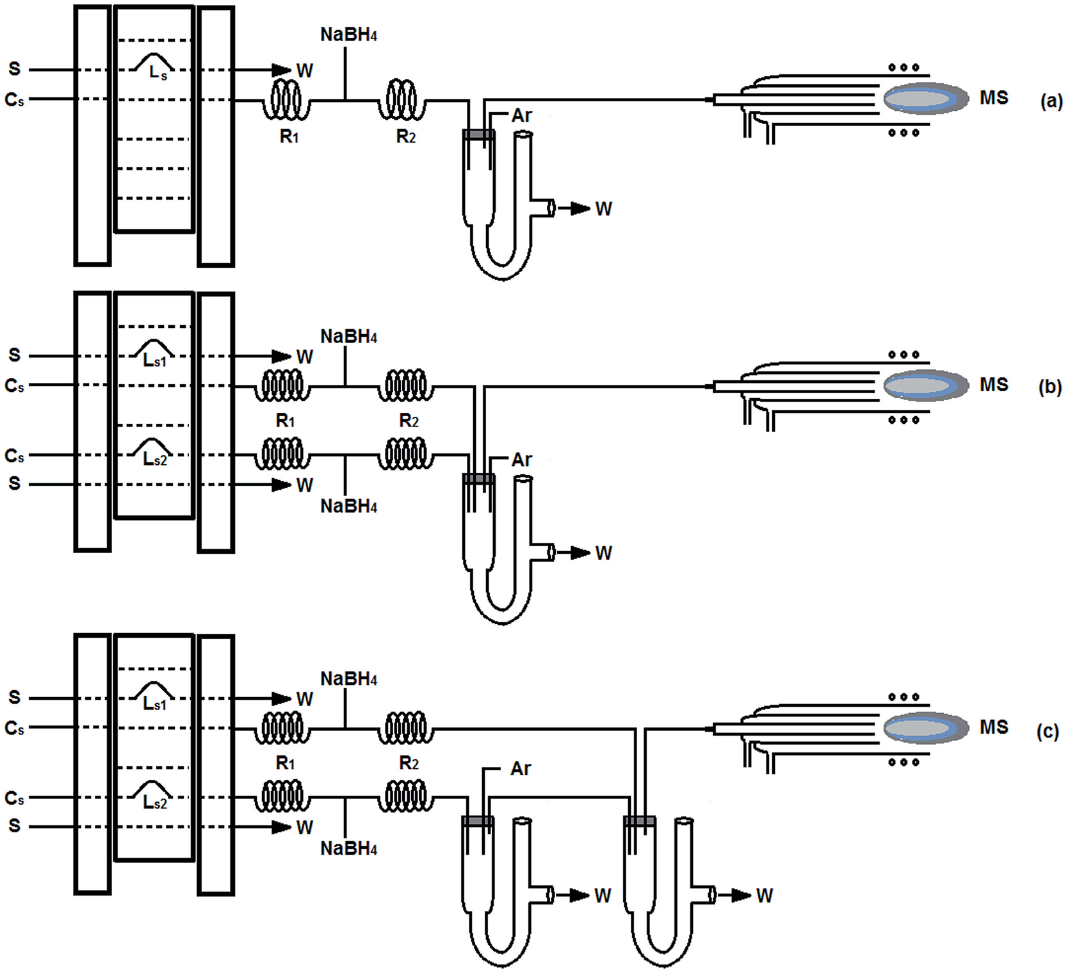

Fig. 1 FI-HG-ICP-MS systems with single (a) and dual channel (b) and (c) with one and two G/L separators, respectively. C_S: sample carrier; R: $NaBH_4$ solution; R_1 and R_2: reaction coils; S: samples or standards; L_{s1} and L_{s2}: sample loop; G/L: gas/liquid separator; Ar: carrier gas; MS: mass spectrometer; W: waste.

order to overcome possible interference from the sample matrix.

For each FI system, the conditions were adjusted in order to overcome interference and consequently allow the determination of analytes by using external calibration. As no certified reference material for the lead alloy was available in the laboratory, analyte recovery tests were carried out. The analytes were added before sample decomposition. The amount added of each element was set in order to have a final concentration of 40.0 μg L^{-1} for As, Bi, Sb, Se and Te, and 20.0 μg L^{-1} for Sn in the solution to be measured. These values were chosen according to the approximate concentrations of the elements in the sample solution. For Bi only, the sample solution was first diluted 200-fold. For comparison of results, the elements were also determined by ICP OES.

3. Results and discussion

3.1. Inductively coupled mass spectrometer adjustment

Initially, the ICP-MS instrument was tuned in order to achieve the highest sensitivity for $^{115}In^+$, and oxide ($^{156}CeO^+/^{140}Ce^+$) and double charge ($^{138}Ba^{++}/^{138}Ba^+$) formation lower than 3%, by using the standard mode of operation (pneumatic nebulization). The ion lens voltage was adjusted for using the instrument in "Auto-lens" mode. After tuning the ICP-MS instrument, the FI-HG system (Fig. 1(a)) was connected to the ICP-MS instrument and the carrier gas flow rate and RF power were adjusted in order to obtain the best SBR for the analytes. Hydrochloric acid 1.0 mol L^{-1} (7.4 mL min^{-1}), $NaBH_4$ 0.3% m/v (2.6 mL min^{-1}) and a 5.0 μg L^{-1} standard solution were used. The established conditions for carrier gas flow rate and RF power were 1.25 L min^{-1} and 1300 W, respectively. These conditions were used in subsequent experiments.

3.2. Flow injection system optimization

3.2.1. General considerations in FI system development.

Initial experiments were carried out using a single channel FI system (Fig. 1(a)). The analytical response of the system was evaluated by using standard solutions. The main parameters of the system were studied and the analytes separated into two groups, as described in the next sections. It was observed that

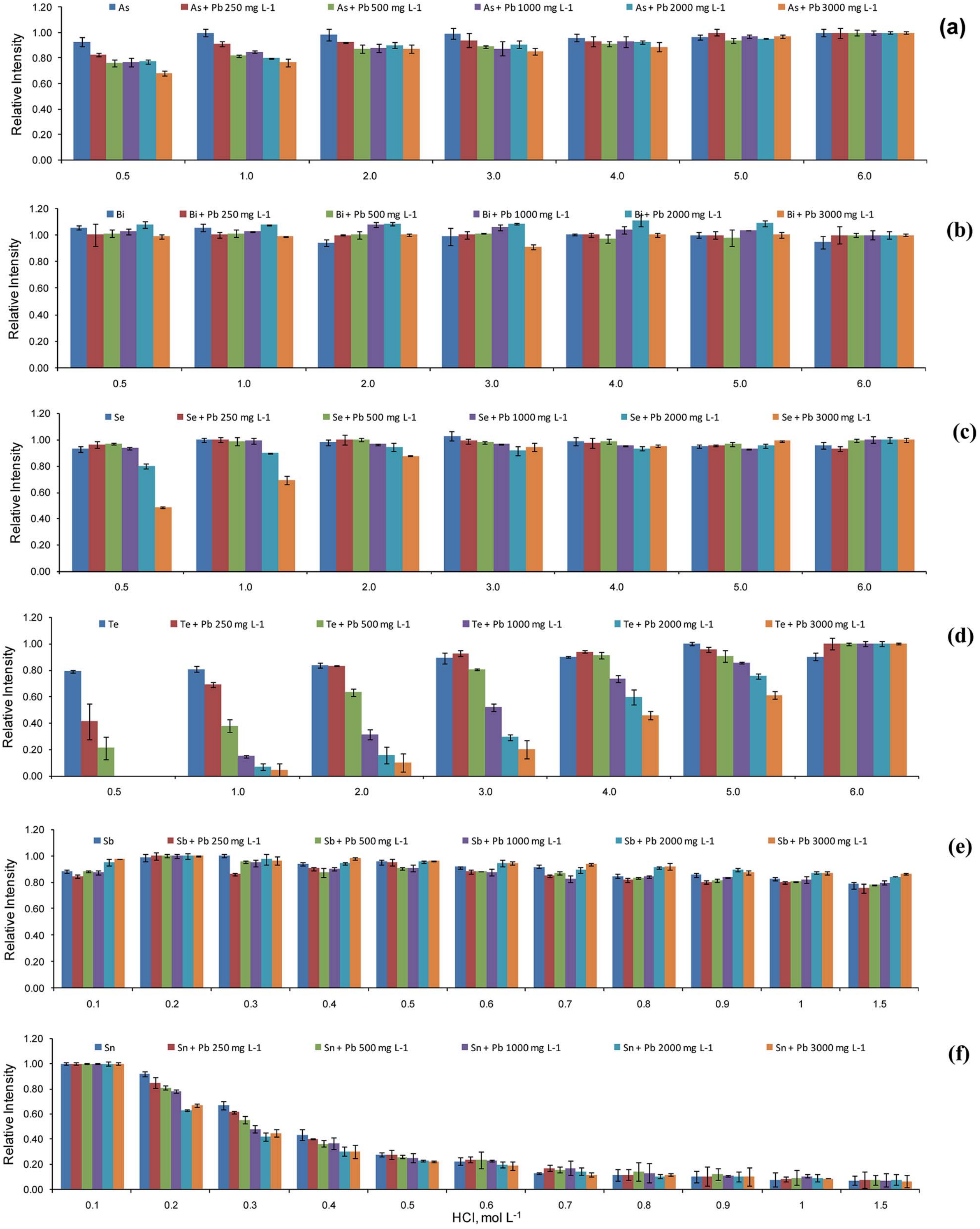

Fig. 2 Effect of HCl and Pb on hydride generation of As, Bi, Sb, Sn, Se and Te. (a)–(d): As, Bi, Se and Te 5.0 μg L^{-1} prepared in 0.5 to 6.0 mol L^{-1} HCl; and As, Bi, Se, Te 5.0 μg L^{-1} plus Pb prepared in 0.5 to 6.0 mol L^{-1} HCl; (e) and (f): Sn and Sb 5.0 μg L^{-1} prepared in water, and Sn and Sb 5.0 μg L^{-1} plus Pb prepared in water; sample carrier flow rate: 7.4 mL min^{-1}; $NaBH_4$ 0.6% m/v solution flow rate: 2.6 mL min^{-1}; Ar flow rate: 1.25 L min^{-1}; sample volume: 90 μL ($n = 3$).

Sb and Sn have similar behaviour in relation to the acid concentration, requiring the use of low HCl concentrations. On the other hand, higher concentrations of HCl should be used for As, Bi, Se and Te. Therefore, it was necessary to separate the elements into two groups. Then, two new FI systems were developed to try to measure all the elements in one run. These FI systems are shown in Fig. 1(b) and (c). Both FI systems consisted of a dual channel with one (Fig. 1(b)) or two (Fig. 1(c)) gas/liquid separators. These systems were evaluated by using the same conditions as those optimized for the single channel FI system. Compromise conditions for the analyte determination, considering the best SBR or conditions where the interference of the sample matrix was overcome, were adopted. After optimization, the effects of the main components of the sample were evaluated, as will be discussed in Section 3.3.

3.2.2. Effect of reagent concentration.

As mentioned before, all parameters were initially evaluated using the FI system shown in Fig. 1(a). Mono-elemental and multi-elemental standard solutions containing 5.0 μg L^{-1} of each element (As, Bi, Sb, Se, Sn and Te) were prepared in water or in 0.5 to 6.0 mol L^{-1} HCl, with the aim of establishing the parameters of the FI-HG system. In order to investigate the influence of the concentration of HCl used as a sample carrier, the concentration of $NaBH_4$ solution was fixed at 0.60% m/v. The flow rate of the sample carrier (HCl) and $NaBH_4$ solutions was fixed at 7.4 and 2.6 mL min^{-1} (see Section 3.2.3), respectively. The sample volume was evaluated and fixed at 90 μL. As can be observed in Fig. 2(a–d), the signal intensity for As, Bi, Se and Te is not affected by increasing the HCl concentration of the sample carrier up to 6.0 mol L^{-1} (standards were prepared in HCl to match the HCl concentration used in each carrier solution). However, a strong effect of HCl concentration in the carrier solution on Sb and Sn signal intensity can be observed in Fig. 2(e–f). An increase in the baseline, poor precision and a decrease in the signal intensity were observed for Sb in the presence of HCl concentrations higher than 1.5 mol L^{-1}. Hydrochloric acid has a more pronounced influence on Sn signal intensity suppression than for the other elements. It is known that stibine and stannane are more efficiently generated under low-acid conditions, typically not higher than about 0.1 mol L^{-1} of acids such as HCl, HNO_3 and $HClO_4$,[13,17] which is in accordance with the results shown in Fig. 2(e–f).

Moreover, the influence of HCl concentration on the preparation of the sample and standards was evaluated. As expected, sample preparation in low HCl concentrations causes Pb precipitation, probably as $PbCl_2$. In addition, as can be observed in Fig. 1(a–f), the presence of Pb affects the hydride formation, with Te being affected most. Therefore, as a compromise condition, 6.0 mol L^{-1} HCl was chosen for As, Bi, Se and Te preparation, while water was used for Sb and Sn.

In view of the different behaviours for hydride generation of the elements in relation to HCl concentration, they were divided into two groups: (i) As, Bi, Se and Te, where the sample carrier and samples and standards were prepared in 6.0 mol L^{-1} HCl, and (ii) Sb and Sn, where 0.1 mol L^{-1} HCl was used as sample carrier and water for sample and standard preparation. Therefore, in order to gain the advantage of the multi-elemental capability of the ICP-MS technique and the versatility of FI systems, two new FI systems (Fig. 1(b) and (c)) were designed and evaluated. By using these systems, hydrides of As, Bi, Se and Te were generated in one channel of the FI system and hydrides of Sb and Sn were generated in the other channel. More details of these systems are given in Section 3.2.4. Separation of the elements into two groups is also important in view of the influence of the sample matrix, as will be discussed in Section 3.3. However, by using the system shown in Fig. 1(b) a black precipitate is formed in the presence of Pb, probably related to elemental lead formation due to its reduction by $NaBH_4$. In spite of this condition, signal suppression of Sb and Sn was observed in the presence of the precipitate only after five to ten sample injections.

As expected, $NaBH_4$ concentration has a strong influence on hydride generation and depends on each element. In general, by using the proposed FI system, the signal intensity of the elements increases with increasing $NaBH_4$ concentration up to 0.50–0.60% m/v (Fig. 3), except for Bi and Sb, where maximum signal intensity is observed at 0.20–0.40% m/v $NaBH_4$. A decrease in signal for all elements is observed when the $NaBH_4$ concentration is higher than 0.70% m/v, probably as a consequence of changes in plasma characteristics due to the high hydrogen production and/or a shift in the analytical zone of the plasma. As a compromise condition, subsequent experiments were carried out using 0.60% m/v $NaBH_4$ solutions. Under these conditions, the signal intensities in the presence of 2000 mg L^{-1} of Pb and in the absence of Pb are essentially equal, thereby avoiding the interference from this element.

3.2.3. Effect of reaction coil length, sample volume and solution flow rates.

Experiments were carried out in order to evaluate the influence of the reaction coil (R_1 and R_2) length, sample volume (L_s) and solution flow rates of the sample carrier (C_s) and reductant ($NaBH_4$) solutions by using the FI system depicted in Fig. 1(a) and the conditions described previously (Section 3.2.2). For these evaluations, reaction conditions were selected according to the two groups previously established.

A good compromise condition for the sample carrier and reductant flow rates was 7.4 mL min^{-1} and 2.6 mL min^{-1}, respectively. The sample volume was 90 μL and the reaction coil R_1 and R_2 length was 40 cm and 100 cm, respectively.

As expected, by increasing the sample volume, the signal intensity increases (measured in peak height) linearly up to a certain value, stabilizing thereafter.[24] However, chemical interferences in HG are related to the quantity (mass) of the interferent present in the reaction system.[15] Therefore, if chemical interferences are observed, they can be circumvented by diluting the sample solution. In FI systems, this can be done by reducing the sample volume injected into the system or by increasing the reaction path (reaction coil R_1 and R_2). Fig. 4 shows the influence of the sample volume used in the FI-HG system (Fig. 1(a)) in the absence and presence of 2000 mg L^{-1} Pb. As expected, the signal intensity increased with an increase in the sample volume of standard solution. However, as can be observed in Fig. 4, 2000 mg L^{-1} Pb interferes with As and Te at sample volumes higher than 140 μL. For Sb and Sn, the maximum volume injected was 140 μL, since with higher

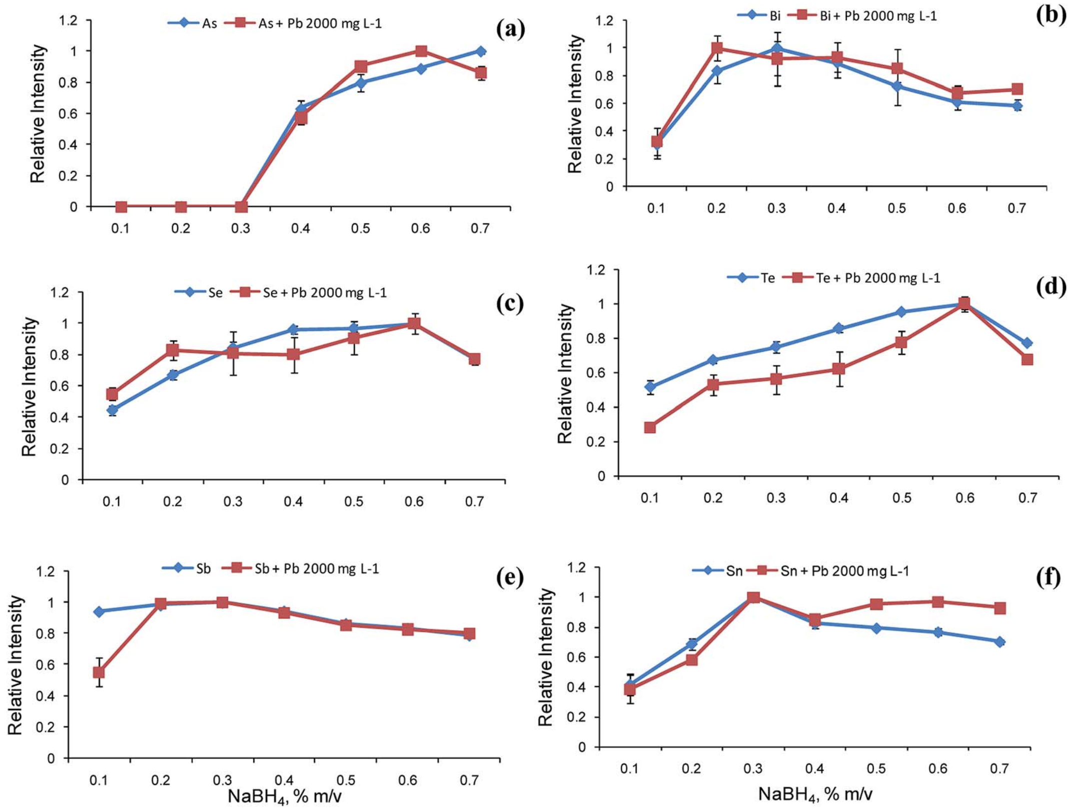

Fig. 3 Effect of $NaBH_4$ concentration on hydride generation of As, Bi, Sb, Se, Sn and Te. (a)–(d): As, Bi, Se and Te 5.0 μg L^{-1} in 6.0 mol L^{-1} HCl; sample carrier (6.0 mol L^{-1} HCl) flow rate: 7.4 mL min^{-1}; (e) and (f): Sb and Sn 5.0 μg L^{-1} in water; sample carrier (0.1 mol L^{-1} HCl) flow rate: 7.4 mL min^{-1}; $NaBH_4$ solution flow rate: 2.4 mL min^{-1}; Ar flow rate: 1.25 L min^{-1}; sample volume: 90 μL (n = 3).

volumes double peaks are formed. The formation of double peaks can be related to the formation of an acid gradient in the sample zone, since the sample carrier is 0.1 mol L^{-1} HCl and the sample is prepared in water. Perhaps the pH of the central zone of the sample does not favour the generation of hydrides when volumes higher than 140 μL are injected. Therefore, the sample volume was fixed at 90 μL for all elements.

The length of the reaction coil R_1 was fixed at 40 cm while the influence of the length of the reaction coil R_2 was evaluated from 50 cm up to 200 cm. Signal intensity remained essentially constant up to 100 cm, whereas it decreased slightly when R_2 was greater than 150 cm. This behaviour was expected, since there is a compromise between the conditions promoting hydride formation and the dissociation or hydrolysis of hydrides when they remain in contact with the solution for a longer period. Similar behaviour was observed by Abrankó *et al.*[22] By increasing the R_1 length, the analyte signal intensity decreases, but no major influence is observed. Therefore, subsequent experiments were carried out using the lengths of R_1 and R_2 fixed at 40 cm and 100 cm, respectively.

3.2.4. Flow injection systems. As mentioned before, the use of the FI-HG shown in Fig. 1(a) is not suitable for determining all the elements simultaneously by using the same reaction conditions. Therefore, in order to make the analysis simpler, the FI system shown in Fig. 1(b) was evaluated. With this system it is possible to determine all the elements in one run by employing the established conditions for each group of elements. That is, hydrides of As, Bi, Se and Te are generated and measured in one channel of the FI system while hydrides of Sb and Sn are generated and measured in the other channel. However, interferences were observed after some sample injections, mainly on Sb and Sn measurements. Probably the interference is related to the acid conditions, since the reaction may occur in the liquid phase in the G/L separator and not only in the reaction coil (R_2). Furthermore, a precipitate is formed in the G/L separator when 2000 mg L^{-1} Pb is present, as pointed out in Section 3.2.2. Therefore, the FI system shown in Fig. 1(c) was developed. In this system, by using two G/L separators it is possible to carry out the hydride generation of As, Bi, Se and Te in one section of the FI system, and the hydride generation of Sb and Sn in the other section, without having contact between the different solutions. By using the FI system with two G/L separators, the six elements can be measured in one run. By using the optimized conditions described previously (Sections 3.2.2 and 3.2.3), no interferences were observed. Therefore, subsequent experiments were carried out using this FI system and the conditions described in Table 1.

3.3. Evaluation of interferences on hydride generation

It is well recognized that several elements (mainly transition metals) interfere in hydride generation.[22] Several approaches

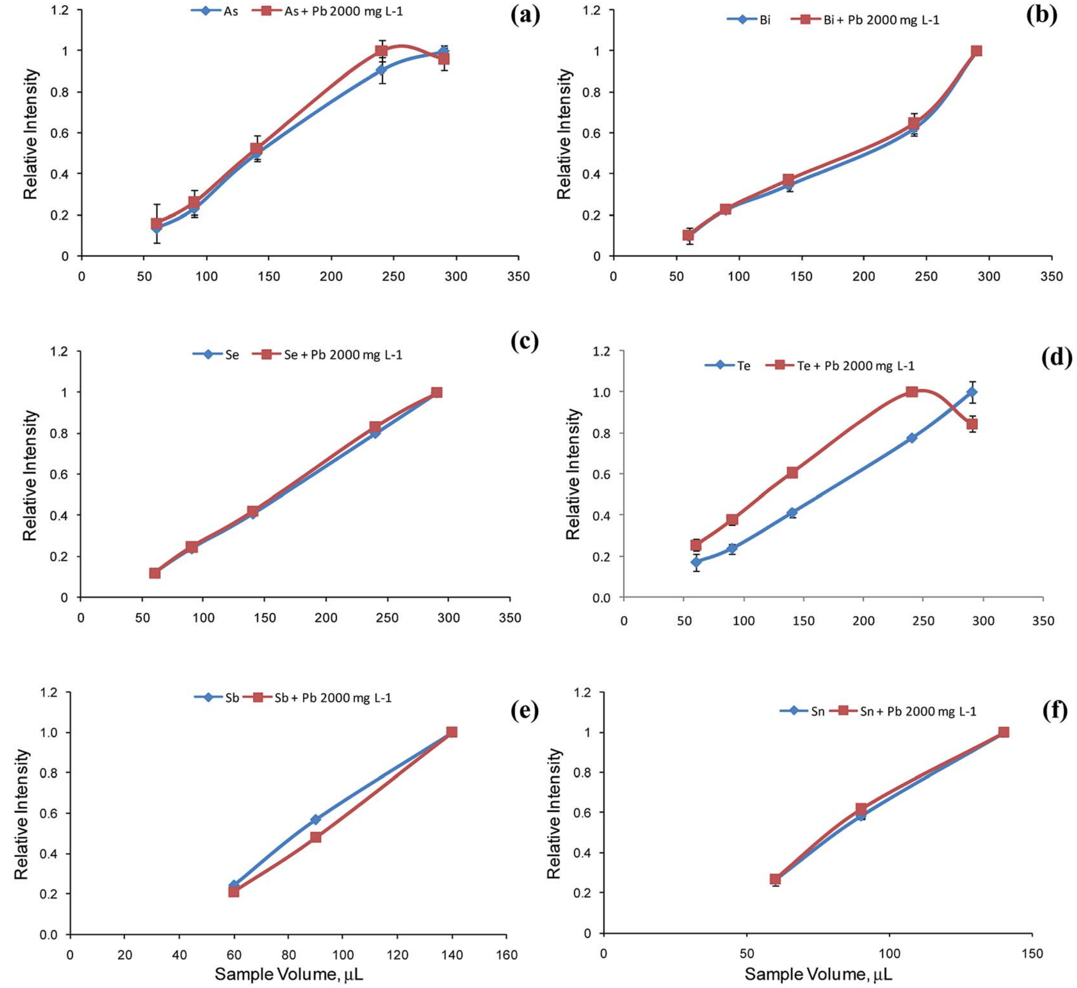

Fig. 4 Influence of sample volume on hydride generation of As, Bi, Sb, Se, Sn and Te. (a)–(d): As, Bi, Se and Te 5.0 µg L^{-1} prepared in 6.0 mol L^{-1} HCl; sample carrier (6.0 mol L^{-1} HCl) flow rate: 7.4 mL min^{-1}; (e) and (f): Sb and Sn 5.0 µg L^{-1} prepared in water; sample carrier (0.1 mol L^{-1} HCl) flow rate: 7.4 mL min^{-1}; $NaBH_4$ (0.60% m/v) flow rate: 2.4 mL min^{-1}; Ar flow rate: 1.25 L min^{-1} ($n = 3$).

can be found in the literature to minimize or overcome these interferences, such as the use of complexing agents, working in the presence of high HCl concentrations and the use of batch or flow systems.[13,20,22] In order to investigate the presence of possible interferences on hydride generation, the sample was first analysed by inductively coupled plasma optical emission spectrometry (ICP OES). In addition to Pb, only Ag and Cu were detected in the samples, concentrations of which were in the order of 40 and 9.0 µg g^{-1}, respectively. The concentrations of Ca, Cd, Fe, Ni and Zn were lower than 0.2 µg g^{-1} and did not interfere in hydride generation at this level. In this way, the influence of Pb, Ag and Cu on hydride generation of As, Bi, Sb, Se, Sn and Te was investigated. The influence of Bi, Sb and Te on the other analytes was also evaluated. All evaluations were carried out using standard solutions containing 5.0 µg L^{-1} of As, Bi, Sb, Se, Sn and Te. The influence of the concentration of the interferent element, sample volume, and HCl and $NaBH_4$ concentrations were investigated. Fig. 2 shows the effects of Pb and HCl concentrations on hydride generation of As, Bi, Se, Sb, Sn and Te. As can be observed, by increasing the HCl concentration, the interference of Pb decreases. This is more evident for Te, and when the Pb concentration is higher. The best condition for Sn is 0.1 mol L^{-1} HCl, where no interference of Pb is observed. The interference of Pb on Sb and Bi up to 3000 mg L^{-1} is not pronounced and does not depend on the HCl concentration. However, in general, the interference from Pb becomes more intense on As, Se and Te for concentrations higher than 2000 mg L^{-1} Pb, being more severe on Te. As compromise conditions, for As, Bi, Se and Te, 6.0 mol L^{-1} HCl was chosen both as the sample carrier and for the sample preparation; and for Sb and Sn, 0.1 mol L^{-1} HCl was chosen as the sample carrier and water was chosen for sample preparation. By using these conditions, it proved possible to determine all elements in the presence of 2000 mg L^{-1} Pb.

The effect of $NaBH_4$ concentration on hydride generation is shown in Fig. 3. As expected, the efficiency of hydride generation is affected by $NaBH_4$ concentration and depends on each element. The influence of 2000 mg L^{-1} Pb on hydride generation in different $NaBH_4$ concentrations was also tested. In general, the interference of 2000 mg L^{-1} Pb is not severe.

Table 1 Parameters of the ICP-MS instrument and for hydride generation by using the FI system

Parameter	Condition
ICP-MS	
RF power, W	1300
Plasma gas flow rate, L min^{-1}	15
Auxiliary gas flow rate, L min^{-1}	1.0
Nebulizer gas flow rate, L min^{-1}	1.25
Sampler and skimmer cones	Pt
Lens voltage, V	Auto lens
Sweeps/reading	1
Readings/replicate	100
Replicates	1
Data collection mode	Peak hopping
Dwell time, ms	15
FI-HG	
Sample carrier solution (HCl), mol L^{-1}	0.1 (Sb, Sn) 6.0 (As, Bi, Se, Te)
Reductant solution ($NaBH_4$),% (m/v)	0.60
Sample carrier flow rate, mL min^{-1}	7.4
Reductant solution flow rate, mL min^{-1}	2.6
Carrier gas flow rate (Ar), L min^{-1}	1.25
Reactor coil length (R_1), cm	40
Reactor coil length (R_2), cm	100
Sample volume, μL	90

However, the best condition is observed when $NaBH_4$ is around 0.60% m/v, the condition chosen for subsequent experiments.

The effect of Ag and Cu on the analyte signal intensity was also evaluated and the results can be seen in Fig. 5. All tests were carried out using standard solutions containing 5.0 μg L^{-1}, where As, Bi, Se and Te were prepared in 6.0 mol L^{-1} HCl and Sb and Sn in water. All solutions were prepared in the presence of 2000 mg L^{-1} Pb. Strong signal suppression of As, Te, Sn and Se was observed in the presence of Ag and Cu at concentrations higher than 500 μg L^{-1}. No interference was observed on Sb in the presence of 2000 μg L^{-1} of Ag and Cu.

Interference of inter-hydride forming elements is reported in the literature.[22] Therefore, the effect of Sb, Bi and Te, present at higher concentrations in the samples, was evaluated. As can be observed in Fig. 5, interference is more severe on Sn in the presence of Bi, Sb and Te at concentrations higher than 500 μg L^{-1}. Bismuth and Te also interfere with Sb. However, the concentration of Bi, Sb and Te in the final solutions of the samples is lower than 500 μg L^{-1}, making it possible to measure all elements without interference.

In summary, by using the FI system shown in Fig. 2(c) and the established conditions, it is possible to determine As, Bi, Sb, Se, Sn and Te simultaneously in lead alloy samples. A typical signal profile for these elements is shown in Fig. 6. As can be observed, the peaks at 10 s correspond to one group (As, Bi, Se and Te) and the two peaks at 30 s refer to the other group (Sb and Sn).

3.4. Analytical parameters and determination of As, Bi, Sb, Se, Sn and Te in lead alloy

The main analytical parameters of the proposed method are described in Table 2. A sample mass of 1000 mg in a final volume of 50 mL was taken into account to estimate the LOQ. The values of LOQ were estimated by considering 10 s, where *s* is the standard deviation of consecutive measurements of 10 blank solutions prepared in the same way as the samples. As

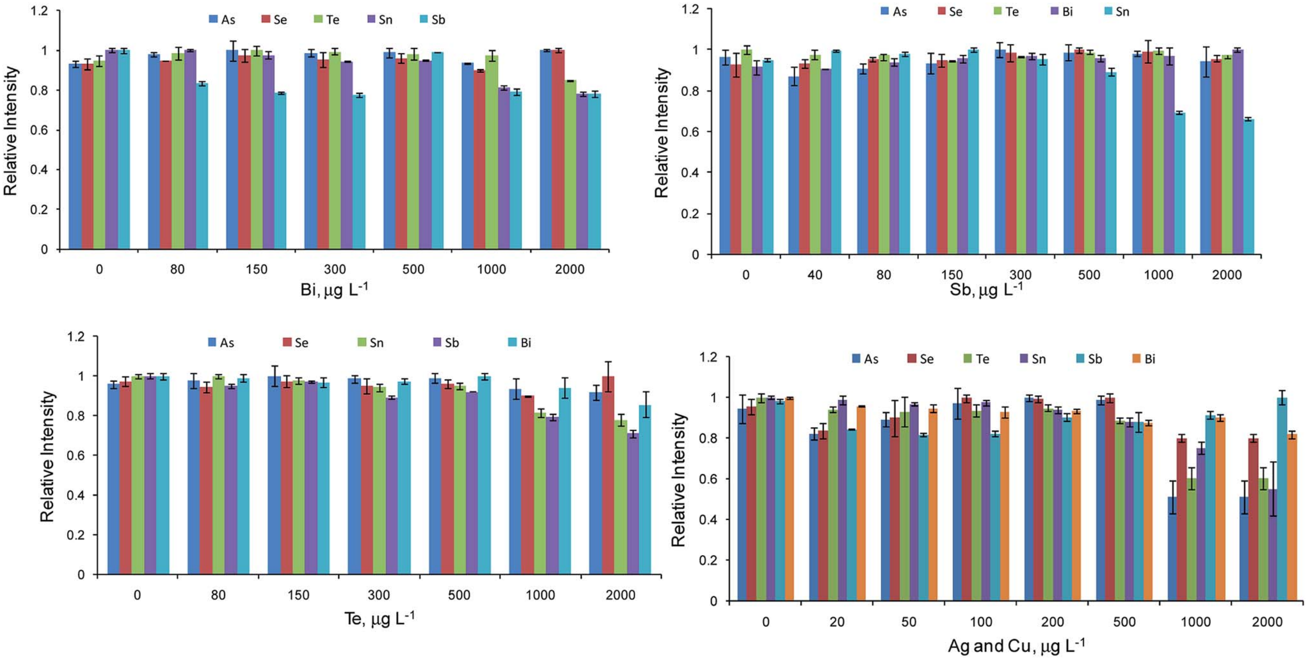

Fig. 5 Effect of Ag, Bi, Cu, Sb and Te on hydride generation. As, Bi, Se and Te: 5 μg L^{-1} in 6.0 mol L^{-1} plus 2000 mg L^{-1} Pb; Sb and Sn: 5 μg L^{-1} in water plus 2000 mg L^{-1} Pb; sample carrier (0.1 mol L^{-1} HCl for Sb and Sn or 6.0 mol L^{-1} HCl for As, Bi, Se and Te) flow rate: 7.4 mL min^{-1}; $NaBH_4$ (0.60% m/v) flow rate: 2.6 mL min^{-1}; Ar flow rate: 1.25 L min^{-1}; sample volume: 90 μL ($n = 3$).

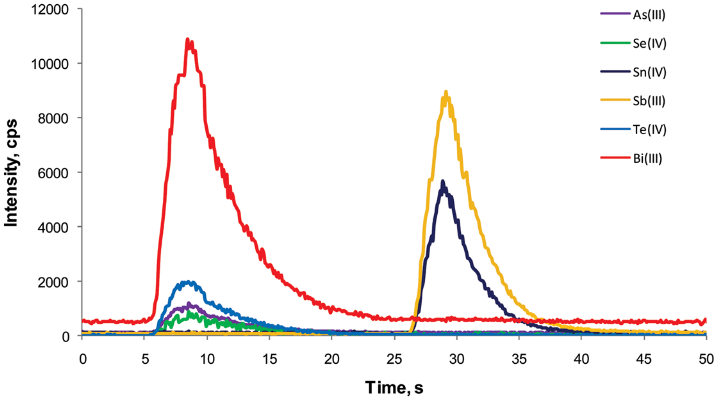

Fig. 6 Signal profile obtained by FI-HG-ICP-MS from a reference solution (0.5 μg L^{-1} As, Bi, Sb, Sn; 50 μg L^{-1} Se; 10 μg L^{-1} Te) by using the FI system shown in Fig. 1(c).

Table 2 Analytical parameters of the proposed method for As, Bi, Sb, Se, Sn and Te determination in lead alloy

	Analytes					
Parameter	As	Bi	Sb	Se	Sn	Te
m/z	75	209	121	82	118	130
Calibration range, μg L^{-1}	1.0–15.0					
RSD,%[a]	7	4	8	6	8	4
LOQ, μg g^{-1}	0.14	0.02	0.03	0.02	0.02	0.02
LOQ, μg g^{-1}[b]	0.50	0.50	0.35	0.50	0.35	0.50
Determinations, h^{-1}[c]	10					

[a] $n = 5$. [b] LOQ for ICP OES. [c] FI system of Fig. 1(c).

can be observed, it is possible to determine the concentrations of all investigated elements at the μg g^{-1} to the ng g^{-1} level in the presence of a high concentration of Pb. The relative standard deviation (RSD for 5 consecutive determinations of the elements in the sample; the RSD of arsenic was determined in the spiked sample) is 8% or lower. Not including the sample preparation step, it is possible to carry out up to 10 measurements per hour by using the FI-HG systems shown in Fig. 1(c).

The proposed method was applied to determine the elements in three lead alloy samples and the results are shown in Table 3. For comparison, the results obtained with the three FI systems are shown. As can be observed, the values obtained by the three systems are similar at a 95% confidence level (*t*-test). The concentration of Bi obtained by the FI system with the dual G/L separators is higher but in good agreement with those obtained by ICP OES (163 ± 11 μg g^{-1}). However, it must be emphasized that the FI system of Fig. 1(c) is more appropriate since it allows the simultaneous determination of the six elements without the problems arising from the formation of precipitate that occurs in the G/L separator of the FI system of Fig. 1(b). It is also possible to determine all the elements using the FI system of Fig. 1(a), but the analysis time is longer, since it is necessary to determine each group of elements separately. Analyte recovery tests were carried out and recoveries were 94 to 101%. The results of Bi, Sb, Se and Te are also in good agreement with those determined by ICP OES. Arsenic and tin were not detected by ICP OES. However, their concentration was measured in spiked samples for which the concentrations of all analytes are in the range of 92 to 98%. The results also show that the valence of As, Sb and Sn has no major influence on hydride generation using the established conditions.

Table 3 Concentration (μg g^{-1}) of As, Bi, Sb, Se, Sn and Te in lead alloy samples determined by the proposed method. The values are the average and standard deviation of three sample replicates[a]

FI system	Sample	As	Bi	Sb	Se	Sn	Te
(a)	A1	<LOQ	144 ± 5	2.4 ± 0.1	0.81 ± 0.03	0.30 ± 0.04	3.1 ± 0.1
	A2	<LOQ	142 ± 3	2.1 ± 0.7	0.70 ± 0.04	0.21 ± 0.04	2.3 ± 0.1
	A3	<LOQ	148 ± 7	3.1 ± 0.1	0.70 ± 0.02	0.20 ± 0.03	3.4 ± 0.1
(b)	A1	<LOQ	140 ± 2	2.6 ± 0.3	0.80 ± 0.10	0.20 ± 0.02	3.4 ± 0.2
	A2	<LOQ	145 ± 2	2.2 ± 0.2	0.90 ± 0.02	0.14 ± 0.05	2.4 ± 0.5
	A3	<LOQ	147 ± 8	3.0 ± 0.1	0.80 ± 0.02	0.20 ± 0.03	3.5 ± 0.1
(c)	A1	<LOQ	173 ± 9	2.3 ± 0.2	0.70 ± 0.10	0.25 ± 0.02	2.2 ± 0.1
	A2	<LOQ	178 ± 5	1.7 ± 0.3	0.90 ± 0.10	0.20 ± 0.02	2.0 ± 0.1
	A3	<LOQ	167 ± 9	3.6 ± 0.2	0.90 ± 0.20	0.30 ± 0.02	3.6 ± 0.2

[a] FI system shown in Fig. 1(a), (b) FI system shown in Fig. 1(b), (c) FI system shown in Fig. 1(c).

4. Conclusions

It was demonstrated for the first time that is possible to determine low concentrations of As, Bi, Sb, Se, Sn and Te in lead alloys used for battery manufacture by hydride generation-inductively coupled plasma mass spectrometry. Three FI systems were evaluated: single channel, and dual channel with one or two G/L separators. Interferences from Pb, Ag and Cu, as well as of Bi, Sb and Te, were circumvented by using appropriate reaction conditions. The dual channel FI system with two G/L separators is more appropriate and allows the determination of all analytes in one run. In view of the reaction characteristics, it was necessary to separate the elements into two groups (As, Bi, Se and Te in one group, and Sb and Sn in the other group). The sample throughput is 10 measurements h^{-1} and the system is suitable for the determination of hydride-forming elements with considerable precision and accuracy in samples with high amounts of Pb.

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