

Assessment of acid media effects on the determination of tin by hydride generation-inductively coupled plasma atomic emission spectrometry

Silvia Farías, Rubén E. Rodríguez, Ariel Ledesma, Daniel A. Batistoni,
Patricia Smichowski*

*Comisión Nacional de Energía Atómica, Unidad de Actividad Química, Centro Atómico Constituyentes, Av. General Paz 1499,
1650-San Martín, Pcia. de Buenos Aires, Argentina*

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Abstract

The effect of several inorganic (nitric, sulfuric and hydrochloric) and organic (acetic, mercaptoacetic and tartaric) acids on the continuous hydride generation determination of tin by ICP-OES was evaluated. The study was aimed to optimize the efficiency of hydride generation as well as the reduction of interference caused by the presence of concomitant elements. Employing reduction with sodium tetrahydroborate, the highest sensitivity was observed with 2.5 M acetic acid. Effects of signal depression produced by transition and hydride-forming elements were less pronounced with acetic and mercaptoacetic acids. Additionally, sensitivity was found to be less dependent on concentration variations for organic acid media. A significant increase in sensitivity was obtained by hydride generation at temperatures above 20 °C. The limit of detection calculated for optimized conditions in acetic acid was 0.1 ng ml⁻¹. Method repeatability was in the 3.1–4.5% R.S.D. range. The accuracy of this method was tested by analysis of a soil certified reference material (GBW 07405).

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1. Introduction

Tin is one of the elements for which its excess burden on the environment [1] is considered of a value comparable to mercury, lead and cadmium. Because it is an essentially non-toxic element, most of the danger posed to ecosystems arises

from organo-alkyl tin species. However, the determination of total tin concentrations at trace levels is required for mass balance calculations in metal fractionation studies of natural samples. Tin is also an element of geochemical interest. In addition, because the metal and its compounds are ubiquitously present in a great deal of industrial processes, such as the manufacturing of glasses, electrically conducting coatings, paints and alloys, a significant increase of tin concentration over

*Corresponding author.

E-mail address: smichows@cnea.gov.ar (P. Smichowski).

baseline values in soils and sediments may be a useful monitor of environment pollution derived from mining and industrial operations.

Relatively few analytical methods for tin are able to reach the low detection limits required in trace analysis. Generation of the volatile covalent tin hydride (stannane) by reaction of metal in solution with a strong reducing agent such as sodium tetrahydroborate, followed by atomic detection (absorption, emission or mass spectrometry) of the evolved metal is usually the method of choice [2–4]. When optimizing the operating conditions, two critical factors should be considered regarding the composition of the acid medium required for hydride formation: first, the effect of the nature and concentration of the acid on the efficiency of the reaction; and second, its possible effect on the masking of interferences produced by concomitant species (mostly transition metals) that might compete with the analyte for reaction with the reductant.

Since the work by Nakahara [5], several studies on the conditions for the continuous generation of the volatile hydride of tin have been reported in the literature, employing quartz tube atomic absorption spectrometry (QT-AAS) as well as inductively coupled plasma-atomic emission spectrometry (ICP-AES) [3,5–8]. Specifically, the effect of varying amounts of strong inorganic acids and some organic acids with complexing properties has been evaluated in Nakahara [5] and Qiu et al. [8].

In this paper we describe the use of continuous hydride generation of stannane followed by ICP-AES detection to evaluate the effect of inorganic and organic acids on the analytical performance of the method. The influence of increasing concentration of hydrochloric, sulfuric, nitric, tartaric, acetic and mercaptoacetic acids was tested regarding the sensitivity for tin determination, as well as in connection with their ability to compensate for interferences originated by the presence of concomitant elements in the sample solution. Besides, some physical aspects related to the volatilization of the hydride have also been addressed. The optimized procedure was applied to the analysis of a certified reference material (Soil GBW

07405). The materials were dissolved by a microwave-assisted dissolution method.

2. Materials and methods

2.1. Instrumentation

The instrumentation and optimized working conditions for the HG-ICP-AES are shown in Table 1. The continuous manifold used to generate the hydride was based on the use of a four channel peristaltic pump (Gilson Minipuls 3, Villiers Le Bel, France), a mixing coil (100 μ l) made of Teflon tubing and a U-tube gas–liquid separator. The cylindrical glass cell (i.d. 2.5 cm) provided efficient separation of the SnH_4 and H_2 from the liquids and mixing of the gaseous products with the carrier gas. The stannane generated was swept out by Ar, which was connected, directly to the inlet tube of the plasma torch. The spray chamber was disconnected and replaced with glass tubing to connect the phase separator with the torch. The transfer line was short enough to avoid transport losses. Details of the instrumental assembly employed are illustrated in Fig. 1.

A Perkin–Elmer atomic absorption spectrometer model 5100 ZL equipped with a Perkin–Elmer Model THGA graphite furnace, a Perkin–Elmer model AS-71 autosampler and a longitudinal Zeeman effect background corrector was used for the study of efficiency. An electrodeless discharge lamp (EDL, Perkin–Elmer) was used as the source of radiation ($\lambda = 286.3$ nm). Pyrolytically-coated graphite tubes with inserted pyrolytic graphite L'vov platforms were employed. High purity Ar (flow rate: 300 ml min⁻¹) was employed to purge air from graphite tubes except during the atomization step, where stopped flow conditions were used. Autosampler volumes of 20 μ l of sample followed by 5 μ l of chemical modifier [5 μ g Pd and 3 μ g $\text{Mg}(\text{NO}_3)_2$] were employed.

A MLS-2000 (Milestone-FKW, Sorisole, Bergamo, Italy) microwave apparatus equipped with Teflon vessels was used to dissolve the soil samples.

2.2. Reagents and standards

All reagents were of analytical reagent grade unless otherwise mentioned. Deionized water from

Table 1
Apparatus and working conditions for HG-ICP-AES

<i>ICP spectrometer</i>	
ICP generator system	HFP-2500 D (Plasma Therm, Kresson, NJ, (USA)
Torch	Ames type, PT 1 (Plasma Therm)
r.f. Power	1.6 kW
Frequency of r.f. generator	27.12 MHz
Coolant gas flow rate	18 l min ⁻¹
Auxiliary gas low rate	0.6 l min ⁻¹
Sample gas flow rate	0.6 l min ⁻¹
Observation height	12 mm
Monochromator	VHR 1000, 1 m focal length (Jobin-Yvon, Longjumeau, France). Interferometric grating: 3600 lines/mm
Analytical line	Sn (I): 289.999 nm
Integration time	4 s
<i>Hydride generation system</i>	
Sample and reagent flow rate	2.3 ml min ⁻¹
Sample acidity	2.5 M acetic acid
NaBH ₄ concentration	0.5%
Coil	100 µl
Tube size (samples and reagents)	1.5 mm (i.d.)

a Nanopure purifier (Sybron-Barnsted, USA) was used throughout. A commercially available 1000 mg l⁻¹ Sn standard solution (Merck, Darmstadt, Germany) was used. Working solutions were prepared daily by serial dilutions of this stock solution. Nitric and hydrochloric acids were prepared by distillation of analytical grade reagents.

A 3.0% (m/v) sodium tetrahydroborate solution was prepared by dissolving NaBH₄ powder (Baker, Phillipsburg, NJ, USA) in deionized water, stabilizing with 0.5% (m/v) NaOH (Merck) and filtering through Whatman N 42 filter paper to eliminate turbidity. The solution was stored in a polyethylene flask at 4 °C. Diluted working solutions were prepared before using.

All solutions containing the potential interferent ions studied were prepared at the required concentrations by adding appropriate amounts of stock solutions made from Merck Titrisol or their chloride salts in 2.5 M acetic acid.

To evaluate the accuracy of the proposed method, portions of the CRM GBW 07405 Soil (Institute of Geophysical and Geochemical Exploration, China) were used.

2.3. Sample preparation

A 0.25-g soil sample was dissolved in the mixture of 5 ml HNO₃ + 4 ml HF + 1 ml HCl applying a multi-step MW-digestion procedure. The average MW power applied during the digestion cycles varied from 300 to 600 W. In all cases the duration of the complete cycle was less than 30 min. The resulting solution was evaporated to almost dryness and the residue dissolved in several milliliters of 2.5 M acetic acid. The solution was filtered and transferred into a 50-ml volumetric flask and filled up with 2.5 M acetic acid. Samples were run by triplicate. Blank solutions were prepared by applying the complete microwave digestion procedure to reagent solutions.

2.4. Procedure

The acidified sample solutions were merged at a Y-piece with the reductant and introduced into the hydride generator as a continuous flow at 2.3 ml min⁻¹ using a peristaltic pump. The SnH₄ generated was separated from the solution in the U-tube separator and swept by Ar (0.6 l min⁻¹)

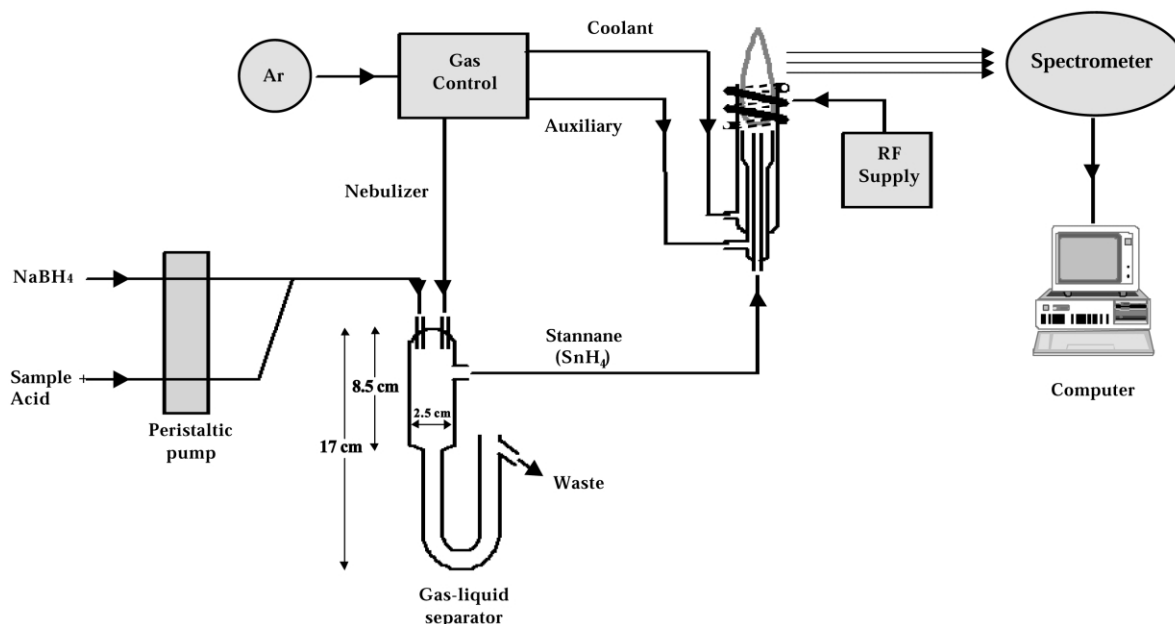


Fig. 1. Schematic diagram of HG-ICP-AES coupling.

directly into the torch (the spray chamber was disconnected).

The lowest blanks were observed when hydrochloric acid was used to generate stannane. The analytical signals obtained were the average of three replicate measurements. The effect of the interferences studied was calculated according to Eq. (1),

$$\% \text{ variation} = [(a - b/b)] \times 100 \quad (1)$$

where a = Sn signal in the presence of interferent and b = Sn signal in absence of interferent.

3. Results and discussion

The efficiency of the hydride generation is strongly dependent on the experimental conditions and the specific instrumental assembly in use. The design of the gas-liquid separator and the optimization of the operating conditions determine the performance of the HG-ICP-AES coupling. Physical and chemical parameters affecting the Sn hydride generation were optimized individually while maintaining the other parameters fixed. Solutions containing 0.2 mg l^{-1} of Sn were used to

optimize the operating parameters in order to obtain the best $I_{\text{Sn}}/I_{\text{b}}$ (ratio of net Sn emission intensity to background emission intensity).

3.1. Chemical parameters

The efficiency of SnH_4 production is a combined function of the acid used, its concentration and the Na-tetrahydroborate concentration. In this study the performance of different acids was evaluated. The parameters tested included: tetrahydroborate concentration and acidity conditions.

Tetrahydroborate concentration: a series of NaBH_4 solutions was prepared covering the range of 0.1–3.0%. The flow rate of both sample acidified with 0.5 M HCl and reductant were 1.5 ml min^{-1} . The tin signal increased continuously with increasing reductant concentration (Fig. 2) up to 0.5%. The decrease of SnH_4 production observed beyond this value is probably due to the large amount of hydrogen gas produced from the reaction of the sodium tetrahydroborate(III) with the acid. A NaBH_4 concentration of 0.5% (m/v) was selected as the more convenient. However, the use

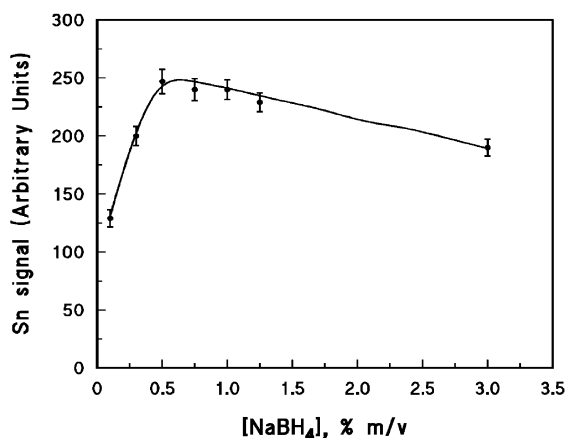


Fig. 2. Effect of NaBH₄ concentration on the Sn signal at concentration of 0.2 mg l⁻¹ applying 0.5 M HCl for acidification of the sample solution.

of relatively low concentrations of tetrahydroborate is advisable in order to reduce blank signals.

Acids and acidity conditions: the efficiency of the generation of SnH₄ is dependent on the acidity at which the reaction is performed and especially on the acid species. The acidity conditions and the acid selected to generate SnH₄ will depend on several factors such as the nature and complexity of the matrix to be analyzed.

The effect of three inorganic and three organic acids on the Sn signal was evaluated. Results of signal variation vs. acid concentration are presented in Figs. 3 and 4. Hydrochloric acid was the first one studied with concentrations ranging between 0.05 and 1.0 M. The Sn signal experienced a sharp maximum (Fig. 3) at approximately 0.2 M HCl. The results in Fig. 3 indicate that the concentrations of nitric and sulfuric acids are also very critical in the determination of tin. Relatively low sensitivity is obtained in the presence of HNO₃ due to the resulting oxidizing medium that compromises the reduction of Sn and consumes the reductant. When inorganic acids are used, stannane can be efficiently generated only in a narrow acidity range and a strict control of pH should be required because small changes around the maximum value may produce a severe decrease in sensitivity. Similar results were reported by

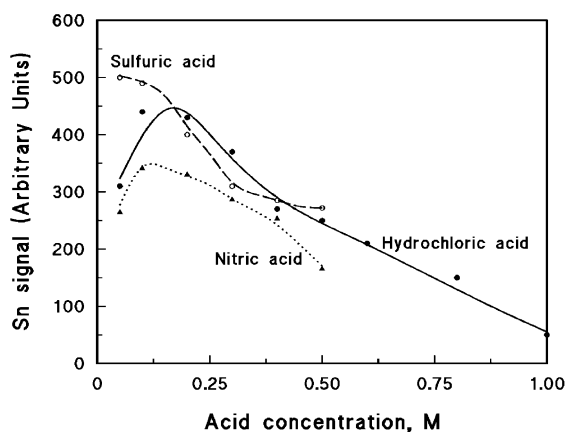


Fig. 3. Effect of HCl, HNO₃ and H₂SO₄ concentrations on the Sn signal at a concentration of 0.2 mg l⁻¹ applying 0.5% (m/v) NaBH₄ solution.

Thompson and Pahlavanpour [9] and Nakahara [5].

When organic acids were tested (Fig. 4), the highest Sn signal was observed with acetic acid. However, SnH₄ production seems to be less dependent on acid concentration and no significant variations were observed between 2.0 and 5.0 M acetic acid. The effects of the other organic reaction media investigated are also depicted in Fig. 4. The signal intensities reached with tartaric and mercaptoacetic acids were lower (especially for mercaptoacetic acid) in comparison with that

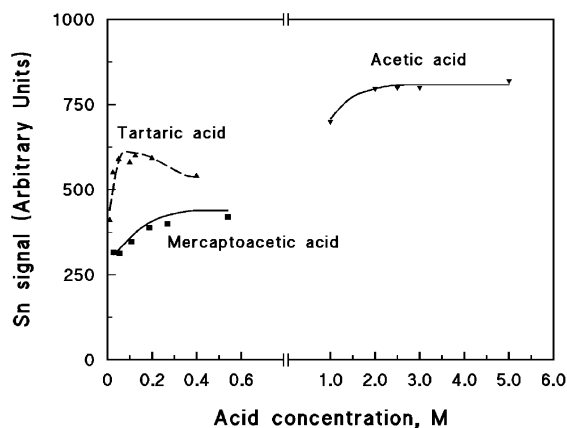


Fig. 4. Effect of acetic, mercaptoacetic and tartaric acid concentrations on the Sn signal.

obtained in acetic acid. The yield of hydride decreased with tartaric acid steadily after a maximum experienced at a 125-mM concentration.

The differences in sensitivities observed among the acids tested may be attributed to changes in the kinetics of the reaction in different media. At higher pH values, in general, a decrease in sensitivity was observed beyond the maximum. This could be explained by a lower reaction rate under such conditions and by SnH_4 dilution in the gas phase due to a higher and faster H_2 production.

3.2. Physical parameters

Physical parameters were optimized using a 0.2-mg l^{-1} solution of Sn, NaBH_4 0.5% (m/v) and acetic acid 2.5 M.

Emission line: the ratio $I_{\text{Sn}}/I_{\text{b}}$ was calculated for three Sn(I) emission lines (nm): 283.999; 242.949; and 235.484. The 283.999 nm wavelength was selected because it gave the best signal to background ratio.

Forward power: the plasma forward power was varied between 1.2 and 1.8 kW and a maximum was experienced at 1.6 kW. This value was used for further work.

Sample and reagents flow rates: to evaluate the effect of the pump rate, the acidified samples and the reductant solutions were pumped (tube i.d. 1.1 mm) at flow rates over the range from 0.8 to 3.0 ml min^{-1} . The experimental data collected in Fig. 5 show that SnH_4 production increased markedly with increasing reagent flow rate at least up to 2.3 ml min^{-1} . This value was chosen as the optimum. Beyond this value, only slight variations in Sn signal were experienced. However, if better detection limits are not required, lower flow rates can be used in order to reduce reagent consumption. When higher pump speeds were tested, the repeatability of the measurements was poorer and precisions higher than 10% were obtained.

Reaction coil volume: the reaction coil serves to provide sufficient delay for completion of the reaction. An optimization of the reaction coil volume is important because a too short reaction coil might cause incomplete hydride release and a too long coil increases risk of interferences in the liquid phase. In this study, a maximum signal was

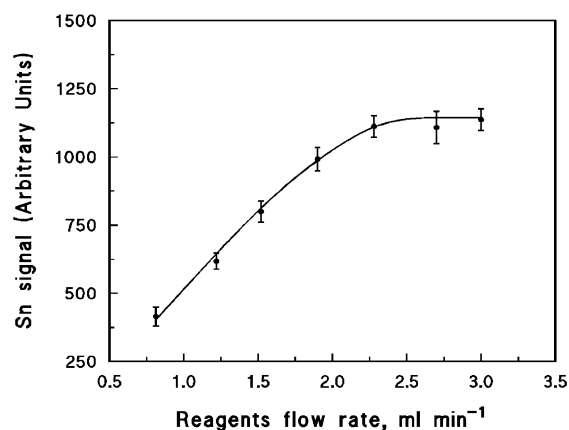


Fig. 5. Influence of sample and NaBH_4 flow rates on the Sn signal, applying 2.5 M acetic acid for acidification.

achieved when coils volume between 100 and $250\text{ }\mu\text{l}$ were tested. A gradual and continuous decrease in SnH_4 evolution was observed when coil volumes higher than $250\text{ }\mu\text{l}$ were employed. A reaction coil of $100\text{ }\mu\text{l}$ was used in subsequent studies.

Transfer line: although not illustrated here, it was found that the Sn signal decreased with increasing connecting tubing length (between the gas–liquid separator and the torch) and for this reason it was as short as possible (approx. 40 cm). When the ratio of transfer lines tested was 1:3 (40 vs. 120 cm) the Sn signal was reduced only 1.4 times. These results confirm that only a slight adsorption of Sn on the wall surface of the connecting tube is experienced.

Argon flow rates: the variation of each one of the three gases flow rates (coolant, auxiliary and sample carrier) with the other two fixed at a constant value was evaluated.

With the coolant and auxiliary gas flow rates fixed, the sample gas flow rate was varied over the range of $0.2\text{--}0.8\text{ l min}^{-1}$ and a maximum was observed between 0.4 and 0.7 l min^{-1} . The carrier gas affects the efficiency of transference and extraction of hydrides from the gas–separator in the hydride generation system. At a lower Ar flow rate the Sn signal decreased significantly probably due to losses by condensation on the surface within the generator. When the Ar flow rate was higher than 0.7 l min^{-1} the Sn signal decreased drastically

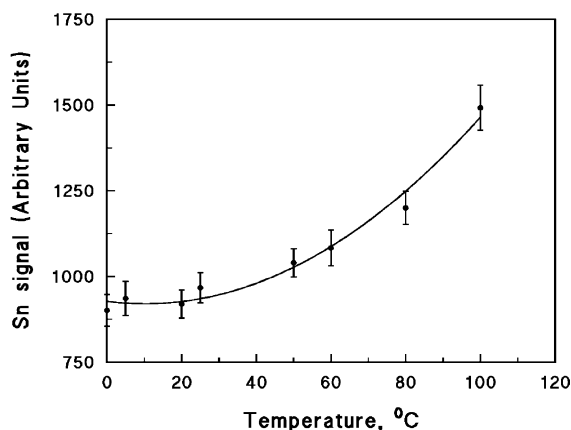


Fig. 6. Influence of temperature on the Sn signal, applying 2.5 M acetic acid for acidification.

due to a shorter residence time of the analyte in the system. The variation in sensitivity observed in the Sn signal may also be attributed to different excitation conditions experienced by the analyte when the Ar flow rate is changed. Besides, a balance between optimum transport efficiency and dilution is reached at 0.6 l min^{-1} . That value was selected for further work.

The effect of variation of the auxiliary gas flow rates between 0.2 and 2.5 l min^{-1} experienced a maximum in the Sn signal at 0.6 l min^{-1} . Below this value a constant decrease was observed that could be explained by an overheating of the inlet tube of the torch, producing premature decomposition of the SnH_4 .

The response of the Sn signal with increasing coolant gas flow rate (10 – 22 l min^{-1}) showed a maximum at 18 l min^{-1} . If the coolant gas flow rate is used at lower values, spectral interferences from molecular species, such as NO, may be expected.

Temperature: in order to evaluate the effect of temperature on SnH_4 generation, the reaction coil was immersed in a water bath and the temperature was varied between 0 and 100°C . The efficiency of hydride generation is low at low temperatures, as it is clearly evident from Fig. 6. The signal increases at higher temperatures up to 100°C , following a second-order relationship with the temperature. The coefficients of the curve adjusted

are as follows: $a_0 = 927.68$; $a_1 = -1.40$; $a_2 = 0.068$. These results could indicate that Sn is transported to the plasma as a stable species. The temperature may be a variable to control in the hydride generation of Sn, because a significant increase ($\approx 60\%$) in sensitivity was observed between 20 and 100°C in our system. In a flow injection–hydride generation–atomic absorption spectrometric method Tsalev et al. [11] observed a sensitivity increase in the tin signal by a factor of two or three at temperatures in the gas–liquid separator of approximately 50 vs. 20°C .

3.3. Efficiency of stannane generation

The efficiency of stannane generation was calculated by quantifying the residual concentration of Sn in the waste of the hydride generator. Measurements were performed by electrothermal atomic absorption spectrometry (ETAAS) under the optimized conditions reported in Section 2.1. Solutions containing $0.2 \mu\text{g Sn ml}^{-1}$ were used to calculate the efficiency of stannane generation and the recovery achieved was 90% .

3.4. Interference study

The determination of Sn by HG coupled to AAS, ICP-AES, ICP-MS and DCP-AES is prone to interferences due to the presence of transition elements and other hydride forming-elements. [5,6,9,10]. The interference effects of metals like Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn on the generation of SnH_4 were studied because these elements compete with the analyte for reduction and catalyze NaBH_4 decomposition. Another group of typical interferents are elements forming volatile hydrides (Periodic groups IV A, V A and VI A). For this reason, the effect of As, Bi, Ge, Pb, Sb, Se, and Te on the Sn signal was evaluated. The effect of Hg on SnH_4 evolution was also observed.

Interference studies in all the reaction media at the optimized working conditions and at the optimal concentration of the acids were investigated. Variations over $\pm 5\%$ in the analytical signal of Sn in the presence of other elements were taken as an interference. All samples analyzed contained 0.2 mg l^{-1} of Sn and the results are the averages

Table 2

Interferences of hydride forming elements and Hg on the analytical signal of Sn obtained by HG-ICP-AES applying different acid media

Ion	Hydrochloric (0.1 M)	Sulfuric (0.05 M)	Nitric (0.1 M)	Tartaric (0.125 M)	Acetic (2.5 M)	Mercaptoacetic (0.550 M)
Sb(III)	–46	–31	–52	–64	–23	–17
Bi(III)	^a *	–51	–69	–89	–35	–21
Se(IV)	–57	–41	–66	–75	–55	–27
As(III)	–52	–47	–54	–14	–28	–10
Pb(II)	^a *	^a *	–80	^a *	–35	–41
Te(IV)	^a *	–71	^a *	–46	^a *	^a *
Ge(IV)	–66	–18	–36	+12	+12	–9
Hg(II)	–46	–37	–41	^a *	^a *	^a *

Concentration of interfering elements, tin and NaBH₄ are 50, 0.2 mg l^{–1} and 0.5%, respectively. Results express the change of the tin signal in percentage.

^a * not measurable because of turbidity or precipitation.

of three measurements. The results of the interference study are summarized in Tables 2 and 3. It can be observed that a number of metal ions react with NaBH₄ to form metal borides or free metal suspensions. Enhancing effects were only observed for Ge (tartaric and acetic acids) and Fe (tartaric acid).

Discrepancies about the effect exerted by diverse elements on Sn signal are frequently observed in the literature. They could be explained by the different generation devices, instrumentation and analytical conditions employed. In spite of that, there is consensus that Sn is in general vulnerable to depressive interferences.

The interferent effect caused by the other hydride-forming elements (Table 2) on Sn signal is more serious and difficult to control in comparison with other elements such as As, Sb, Ge, etc. In our study, Se, Bi, Pb and Te comprised the most serious interfering elements among those investigated.

When the effect of transition metals was evaluated, it is evident from Table 3 that Cu, Co and Ni are serious depressive interferences with the majority of the acid media tested. It must be pointed out that the presence of Cu 50 mg l^{–1} in hydrochloric and nitric acids as well as Co and Ni in nitric acid practically masked the Sn signal.

Table 3

Interferences of heavy metals in the determination of Sn by HG-ICP-AES in various acid media

Ion	Hydrochloric (0.1 M)	Sulfuric (0.05 M)	Nitric (0.1 M)	Tartaric (0.125 M)	Acetic (2.5 M)	Mercaptoacetic (0.550 M)
Cr(III)	–36	–54	–36	–23	–41	–20
Mn(II)	–56	–80	–66	–40	–22	–14
Co(II)	–67	–80	–91	–25	–14	–16
Cd(II)	–21	–67	–50	–20	–16	–17
Cu(II)	–92	–45	–89	–33	–12	–17
Zn(II)	^a *	^a *	^a *	0	^a *	–12
Ni(II)	–84	–57	–92	–14	–22	–22
Fe(III)	–68	–29	–42	+11	–18	–19

Concentration of interfering elements, tin and NaBH₄ are 50, 0.2 mg l^{–1} and 0.5%, respectively. Results express the change of the tin signal in percentage.

^a * not measurable because of turbidity or precipitation.

Table 4
Analytical performance for the Sn determination as SnH_4

Acid and molarity	Detection limit (3σ) ^a (ng ml ⁻¹)	Precision (%) ^a (for 0.2 mg Sn l ⁻¹)
Hydrochloric (0.1 M)	0.3	4.5
Sulfuric (0.05 M)	0.4	3.9
Nitric (0.1 M)	0.5	4.4
Tartaric (0.125 M)	0.4	3.8
Acetic (2.5 M)	0.1	3.4
Mercaptoacetic (0.550 M)	0.4	3.1

^a ($n=10$).

Only Fe at 50 mg l⁻¹ enhanced the Sn signal when tartaric acid was employed as the reaction media.

A composite picture of Tables 2 and 3 indicates that in general terms, acetic and mercaptoacetic acids reduced the adverse effects of hydride forming elements and transition metals on Sn signal. However, the reduction of Sn to stannane was more efficient in acetic acid (Fig. 4) and for this reason it was selected as the acidic reaction media for analyzing the samples.

3.5. Analytical performance

The acids studied were also compared in terms of their quality parameters as a preliminary step to the determination of Sn in a soil certified reference material by HG-ICP-AES. Using optimized conditions, analytical figures of merit including, detection limit and precision of replicate measurements were established.

The detection limits were calculated following the IUPAC rules [12] on the basis of 3σ criterion for 10 replicated measurements of the blank signal. Results averaged between 0.1 and 0.5 $\mu\text{g l}^{-1}$ (Table 4) depending on the acid studied. Precision was evaluated for the six acids using a standard containing 0.2 $\mu\text{g l}^{-1}$ of Sn and the values of % RSD obtained were in the range of 3.1–4.5 for 10 replicate measurements. Results are set forth in Table 4. Compared with conventional continuous nebulization the coupling HG-ICP-AES gives a sensitivity increase of a factor of approximately two orders of magnitude. In all cases, the linear

calibration curves ranged approximately four orders of magnitude.

3.6. Analysis of a soil certified reference material

From the above described study, it can be concluded that mercaptoacetic and acetic acids are both suitable reaction media to reduce interferences to some extent. However, due to the lower sensitivity obtained with mercaptoacetic acid and its higher toxicity, acetic acid was selected as the best alternative.

To check the accuracy of the optimized HG-ICP-AES method the Sn concentration was determined in a soil certified reference material (GBW 077405). Three sub-samples were analyzed applying the calibration curve determined with standard solutions containing acetic acid in concentrations of 2.5 M. The certified concentration value ($18 \pm 4 \mu\text{g/g}$) shows a good agreement with the measured concentration data ($20.8 \pm 1.4 \mu\text{g/g}$).

4. Conclusions

ICP-AES in conjunction with HG is fully able to determine Sn at trace levels in environmental samples as soils. The effects of hydrochloric, nitric, sulfuric, tartaric, mercaptoacetic and acetic acids at different concentrations on the efficiency of SnH_4 generation were evaluated. Although with all the acids studied stannane is evolved within a certain acidity interval, organic acids should be preferred as reaction media because their dependence on concentration is less critical in comparison with inorganic acids. Interferences are reduced to

some extent, possibly due to the formation of complexes. The best operating conditions, in terms of sensitivity and control of interferences are obtained with acetic and mercaptoacetic acids.

The detection limit of the optimized method developed was improved by two orders of magnitude in comparison with conventional continuous nebulization.

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References

- [1] E.-I. Ochiai, *J. Chem. Educ.* 72 (1995) 479.
- [2] J. Dedina, D.L. Tsalev, Tin, in: J. Wiley (Ed.), *Hydride Generation in Atomic Absorption Spectrometry*, Ch. 16, 1995, p. 372.
- [3] Y.-L. Feng, H.-W. Chen, H.-Y. Chen, L.-C. Tian, *Fresenius J. Anal. Chem* 361 (1998) 155.
- [4] L.S. Zhang, S. Comb, *J. Anal. At. Spectrom.* 11 (1996) 1043.
- [5] T. Nakahara, *Appl. Spectrosc.* 37 (1983) 539.
- [6] J.R. Castillo, J.M. Mir, I. Pérez, *Microchem. J.* 39 (1989) 119.
- [7] X.-C. Le, W.R. Cullen, K.J. Reimer, I.D. Brindle, *Anal. Chim. Acta* 258 (1992) 307.
- [8] D.R. Qiu, C. Vandecasteele, K. Vermeiren, R. Dams, *Spectrochim. Acta* 45B (1990) 439.
- [9] M. Thompson, B. Pahlavanpour, *Anal. Chim. Acta* 109 (1979) 251.
- [10] I.D. Brindle, X.-C. Le, *Analyst* 113 (1988) 1377.
- [11] D.L. Tsalev, M. Sperling, B. Welz, *Analyst* 117 (1992) 1729.
- [12] J.D. Winefordner, G.L. Long, *Anal. Chem.* 55 (1983) 712A.