



Hydride generation in-atomizer collection atomic absorption spectrometry for the determination of antimony in acetic acid leachates from pewter cups

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ABSTRACT

Antimony is one of the constituents of pewter, an alloy composed of a minimum of 90% tin with the balance being made up with copper, antimony and perhaps some bismuth. A method has been developed to determine Sb in acetic acid leachates from pewter cups. The employed instrumentation, an atomic absorption spectrometer, equipped with a quartz trap-and-atomizer device, is simple and relatively inexpensive with low running costs. Interferences due to the presence of tin and ways to control them were investigated in detail. The applied approach made possible to overcome potentially serious interference of Sn leached from the cup material (which was shown to take place in the atomizer), by a combination of (i) high concentration of HCl, which decreases the efficiency of stannane generation and (ii) in-atomizer collection. The resulting Sn tolerance limit was between 10 and 20 mg L⁻¹. The advantages of the in-atomizer collection are a lower tin interference in the atomizer, and a much better limit of detection (LOD), which makes possible reducing the atomization interference further by working with more diluted sample solutions. Besides the Sn interference, an interference of an unknown volatile compound transported to the atomizer together with stibine was identified in the measured sample solutions. This interference could be controlled using the analyte addition technique. The applicability of the method was tested on solutions containing a wide range of interferents leached from the pewter cups, obtained at leaching times between 1 and 24 h. The LOD in the sample solutions was found to be 0.03 µg L⁻¹ Sb.

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1. Introduction

Industrial consumption of antimony steadily increases; it is used in semiconductor industry to produce diodes and Hall-effect devices. Moreover, this metal is also contained in many alloys since it improves the hardness and mechanical strength of lead-based alloys. Antimony contained in semiconductors, batteries and alloys is usually recycled after the end of working life of the product. However, antimony trioxide which has found many uses in brake linings and as a flame retardant in textiles, papers and plastics, is never recycled from the final products and thus is released in the environment [1]. As a result, the human exposure to antimony and its compounds is increasing. Since Sb has no known biological function, but has been proven to be toxic, there is concern about its long-term effects. Sb₂O₃ is a suspected human carcinogen and is listed as a priority pollutant by the United States Environmental Protection Agency and European Commission [2].

Despite its toxicity, antimony is used in therapeutic agents against major tropical diseases, and also in kitchenware and food industry.

Antimony is part of pewter, an alloy used for kitchenware, tableware, drinking cups etc. Today the composition of pewter for domestic use is rigidly controlled, based on British and European standards, specifying a minimum of 90% tin with the balance being made up of copper, antimony and perhaps some bismuth [3]. Pewter was part of everyday's life until the 19th century. Eating, drinking, celebrating, lighting rooms and taking communion all required long-lasting, affordable objects. Nowadays pewter is enjoying a renaissance worldwide, and its use is growing every year; both, consumers and craftsmen, have rediscovered the beauty and practical function of fine pewter. Pewter production is a very important source of income for São João del-Rei, a Brazilian city situated in the state of Minas Gerais, which is one of the major production centers of pewter artifacts in Latin America [4]. Due to the common use of pewter as a kitchenware, etc., Sb frequently comes into contact with food and beverages. Krachler and Shotykh [5] reported the leaching of relatively high concentrations of Sb from pocket flasks made of pewter. Considering the increasing use

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of pewter kitchenware in some regions of Brazil, it is of great importance to evaluate the leaching of potentially toxic metals from these utensils. The leaching is obviously controlled by the pH and chemical composition of the material that comes into contact with pewter, and probably the most acid solutions that have to be considered in this context, are vinegars.

Hydride generation atomic absorption spectrometry (HG AAS) [6–8] is widely used for the trace determination of many important analytes such as As, Se, Sb, Bi, Pb, Sn, etc. due to its simplicity, sensitivity and selectivity. One of the inherent advantages of generation of volatile forms of analyte for analytical atomic spectrometry is that the analyte can be easily preconcentrated either in a special collection device or directly in the atomizer [8]. As a consequence, reasonably low detection limits (LOD) can be obtained even with simple HG AAS setup, offering an alternative to laboratories equipped with expensive instrumentation such as inductively coupled plasma mass spectrometry (ICP-MS). The most convenient way of preconcentration of hydride forming elements is in-atomizer collection in graphite furnaces or in quartz atomizers. In situ collection in graphite furnaces is a well established and mature technique [9–11]; however, collection in quartz atomizers can be performed with much simpler instrumentation [8,11,12]. Antimony species can be trapped and subsequently volatilized with a preconcentration efficiency of 100% using a compact quartz trap-and-atomizer device as demonstrated recently [13,14]. This device is the multiatomizer [15,16] with its inlet arm modified to serve as the trap and to accommodate the oxygen delivery capillary employed for burning the hydrogen in the trapping step.

The aim of this work was to explore capabilities of the analytical method based on an atomic absorption spectrometer equipped with the quartz trap-and-atomizer device for determination of Sb traces in acetic acid leachates from pewter vessels containing extremely high concentrations of tin. This instrumentation was chosen because of its inherent simplicity and low investment and running costs. As a consequence of the corrosive nature of the leaching solution, high concentrations of metals composing the pewter, especially of tin, were expected in the leachates to be analyzed. Tin interferences were therefore explored in detail and ways to control them were investigated. The applicability of the method for determination of total inorganic Sb was tested on leachates containing a wide range of interferents leached from the pewter cups, using leaching times between 1 and 24 h.

2. Experimental

2.1. Reagents

Analytical grade reagents were used exclusively. Deionized water ($0.2 \mu\text{S cm}^{-1}$, Ultrapure, Watrex, USA) was used to prepare solutions. Working standards were prepared from 1 g L^{-1} Sb stock solution (BDH Laboratory Reagents) by dilution in 1 mol L^{-1} HCl (Merck). The reductant solution was 0.5% (m/v) solution of NaBH_4 (Sigma) in 0.4% (m/v) KOH (Merck), filtered after preparation and stored frozen. 0.5% (m/v) ascorbic acid (Riedel-deHaën) and 8.0% (m/v) KI (Riedel-deHaën) were used as pre-reductant. Sn standards were prepared from a 1 g L^{-1} Sn(II) stock solution (BDH Laboratory Reagents). 99% (m/v) glacial acetic acid (p.a., Lachema Brno, Czech Republic) was used to prepare 3% (m/v) acetic acid (HAc) for leaching of the pewter cups (see below). 38% (m/v) hydrofluoric acid (p.a., Spolchemie, Ústí nad Labem, Czech Republic) was used to clean the trap-and-atomizer device. Working modifier solution for graphite furnace AAS measurements was prepared from 10 g L^{-1} $\text{Pd}(\text{NO}_3)_2$ stock solution (Merck) in 10% (m/v) HNO_3 .

2.2. Leaching procedure and preparation of solutions

A solution containing 3% HAc, prepared from glacial HAc was used as leaching solution for two different pewter cups from the same manufacturer – Marguel (São João del Rei, MG, Brazil). The cups differed in type (with or without solder) and size. The volume capacity of the cup with solder was 300 mL and that without solder was 30 mL. The cups were first washed with deionized water and then filled with the acid solution. The solution in the cup was not stirred during the leaching period. Aliquots of approximately 7.5 and 75 mL were taken out after 1, 3, 12 and 24 h for cups without and with solder, respectively. The solutions, termed leachates in the following text, were transferred to polyethylene flasks and stored in a refrigerator until the analysis.

If not stated otherwise, sample solutions were prepared from the leachates by 1 + 4 dilution in 6 mol L^{-1} HCl. All sample solutions were pre-reduced for 30 min before the analysis by adding solid KI and ascorbic acid to reach their final content of 8% and 0.5% (m/v), respectively. For the analyte addition technique, appropriate mass of Sb in a small volume of 1 mol L^{-1} HCl was added to the leachate before the dilution.

If not stated otherwise, antimony standards containing 1 or $2 \mu\text{g L}^{-1}$ Sb were prepared either (i) in 1 mol L^{-1} HCl or (ii) in a mixture of 0.1 mol L^{-1} HAc and 0.8 mol L^{-1} HCl or (iii) in a mixture of 0.1 mol L^{-1} HAc and 6 mol L^{-1} HCl. The HAc concentration of 0.1 mol L^{-1} corresponds to that in 5 times diluted leachates. Blanks were prepared in the same way as the standards but without adding Sb. The model solutions, used for the interference study, were prepared in the same way as Sb standards or blanks. In addition, they contained between 0.002 and 40 mg L^{-1} Sn. Different concentrations of HCl were added to some of the model solutions. Standards, blanks and model solutions were also pre-reduced with KI and ascorbic acid, following the same procedure as described above for sample solutions (diluted leachates).

2.3. HG AAS setup

An in-house made continuous flow system, similar to that described in Ref. [17], was employed to generate hydrides. Peristaltic pump (Ismatec) flow rates were 4.0 mL min^{-1} for sample and standards, 1.2 mL min^{-1} for reductant solution and 6.0 mL min^{-1} for waste from the gas–liquid separator (GLS). GLS was made from an open quartz tube, with an inner volume of 3 mL, ending with a female standard joint. This was connected to a quartz piece formed by a male standard joint with the gas outlet tube. Argon carrier at a flow rate of 75 mL min^{-1} was used to transport hydrides out of the gas outlet tube of the GLS. A PTFE tape was placed over the male standard joint of the connecting piece to reduce aerosol content in the gaseous phase transported from the outlet tube of the GLS to the trap-and-atomizer device (Fig. 1) described in detail in Ref. [18]. The core of the device is actually a modified T-shaped quartz multiatomizer [15,16] consisting of inlet arm and horizontal arm. The horizontal arm is made of two concentric tubes. The inner tube (optical) is evenly perforated with 14 holes. A flow of 25 mL min^{-1} of air was employed as outer gas, flowing between the two tubes through the holes into the optical arm, continuously throughout the whole procedure. The commercial heating unit with temperature control produced by RMI (Lázně Bohdaneč, Czech Republic) was used to heat the horizontal arm to 900°C during whole procedure (trapping and volatilization steps). The 4-cm section of the inlet arm from the T-junction is covered by the heating unit. The inlet arm is resistively heated independently of the horizontal arm. A silica capillary (0.53 mm i.d.) centered in the inlet arm serves for the oxygen delivery. The oxygen-delivery capillary is interfaced to the inlet arm by means of a polypropylene T-piece fitted to the inlet arm. The right arm of the T-piece (Fig. 1) serves to introduce gases

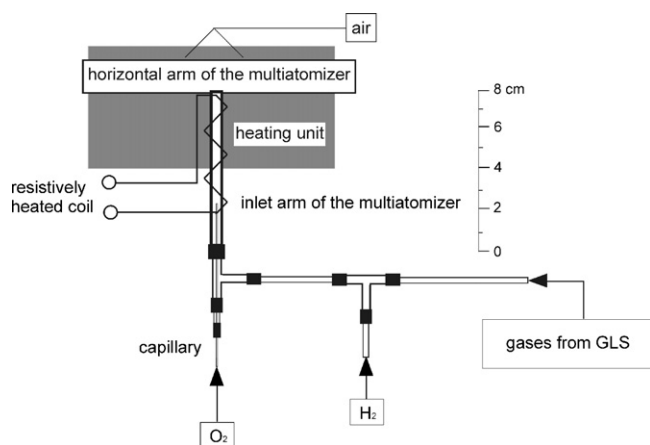


Fig. 1. Schematic diagram of the trap-and-atomizer device.

from the GLS. An additional polypropylene T-piece is inserted into the gas line between GLS and the right arm of the “oxygen channel” T-piece (Fig. 1) to introduce hydrogen from a gas container.

Mass flow controllers (FMA-2600 series, Omega Engineering, USA) were used to regulate flows of Ar, H₂, O₂ and air. The Varian model SpectrAA300/400 atomic absorption spectrometer (Varian, Australia) equipped with Varian Sb hollow cathode lamp operating at 217.6 nm line and 10 mA with 0.2 nm spectral bandpass was employed without background correction.

When a significant loss of sensitivity was observed, the trap-and-atomizer device was disjoined and the quartz part was immersed in a mixture of concentrated HNO₃ and HF (7+3) for 10 min; then it was rinsed with deionized water and let to dry.

2.4. HG AAS procedure

Hydride generation was performed in the direct transfer mode, i.e. hydrides released from measured solutions were directly transported to the trap-and-atomizer device, which was operated either in the on-line atomization mode or in the in-atomizer collection mode.

In the on-line atomization mode, the hydride was transported to the trap-and-atomizer device with unheated inlet arm, opened hydrogen channel, i.e. with a H₂ flow rate of 75 mL min⁻¹, and closed oxygen channel. In effect, with the only exception of the H₂ flow, the trap-and-atomizer device performed in the same way as the previously described multiatomizer [15,16], and the Sb signal was continuously monitored.

The collection mode consisted of two steps: trapping, in which the analyte was retained in the inlet arm of the trap-and-atomizer device, and volatilization/atomization, in which the trapped analyte was released and transferred to the optical tube. The inlet arm temperature was maintained at 900 °C during the whole procedure.

For trapping of the analyte, the oxygen channel was opened to deliver a flow rate of 10 mL min⁻¹ to the capillary and the peristaltic pump was switched on. The introduction time, i.e. the time of pumping the solution for measurement (standard, blank, model or sample solution) to the sample channel, was 30 s corresponding to 2 mL of solution introduced to the hydride generator. Only in some cases an introduction time of 300 s, corresponding to 20 mL of solution for measurement, was used. Then the measured solution was replaced by the blank for 30 s to flush the system. The introduction of oxygen in the stoichiometric excess over hydrogen evolved from the NaBH₄ decomposition (ca 15 mL min⁻¹) resulted in an ignition of a flame burning at the tip of the capillary. The pump was stopped and the oxygen channel was closed at the end of the trapping step.

For the volatilization and atomization of the analyte the H₂ flow of 100 mL min⁻¹ was switched on. Simultaneously with opening the hydrogen channel, the signal of the volatilized analyte atomized in the optical tube was recorded and integrated for 10 s.

2.5. GF AAS measurements

Varian SpectrAA 30 atomic absorption spectrometer equipped with a Zeeman-effect background correction system and DS 15 data station was used. Varian Sn hollow cathode lamp at 286.3 nm line, 0.5 nm spectral bandwidth, operated at 7 mA was the radiation source. A longitudinally heated graphite tube without platform was used. 5 µL of modifier solution containing 100 mg L⁻¹ Pd(NO₃)₂ was added to each replicate. 10 µL of sample or standard solution in 0.1 mol L⁻¹ HAc matrix was injected. It was found that the slope of the calibration curve was not significantly different when preparing standards in 0.1% (m/v) HNO₃ and 0.1 mol L⁻¹ HAc, respectively; hence, the latter matrix was used for standard and sample solutions. The solutions were dried (5 s at 85 °C, 40 s at 95 °C and 10 s at 120 °C), thermally pretreated for 8 s at 500 °C and atomized at 2600 °C (3.2 s). The tube was cleaned at the same temperature for additional 2 s. An argon flow rate of 3 L min⁻¹ was used throughout the program except in the atomization step when gas stop conditions were used.

2.6. Conventions

Peak areas of AAS signals (integrated absorbance) have been invariably employed as the analytical quantity. If sensitivity is mentioned it always stands for peak area related to the analyte mass taken for the measurement. The relative sensitivity means the ratio of sensitivity in the measured sample or in the model solution to that in the standard prepared in the same acid mixture. Averages of at least 3 replicates of peak area values are presented in figures and in the text. Uncertainties are presented as ± standard deviation.

3. Results and discussion

3.1. Optimization of stibine generation – effect of acetic acid

The previously optimized conditions for the generation of stibine from 1 mol L⁻¹ HCl media followed by the on-line atomization [13] were employed in this work as a reference. It should be highlighted that the H₂ flow rate of 75 mL min⁻¹ was invariably used to achieve the same gas flow rates as in the volatilization/atomization step of the in-atomizer collection mode. The corresponding sensitivity (reference sensitivity), expressed as the characteristic mass (*m*₀), defined as the mass of analyte corresponding to an integrated absorbance of 0.0044 s, was found as 22 ± 2 pg within a time interval of several months. Sensitivity observed for the in-atomizer collection mode in the case of generation from 1 mol L⁻¹ HCl media did not differ significantly from the reference sensitivity confirming that the preconcentration efficiency (defined as the ratio of the peak area of the collection mode signal to that of the reference signal [13]) was essentially 100%. Both, *m*₀ and preconcentration efficiency, agree well with our previous measurements [13].

Experimental conditions were optimized with respect to the HAc matrix used in this study. Taking into consideration the dilution of the leachates prior the Sb determination (refer to Section 2.2), the mixture of 0.1 mol L⁻¹ HAc and 0.8 mol L⁻¹ HCl was chosen to test the effect of HAc on stibine generation. Antimony signals in a model matrix of HAc/HCl mixture, spiked with 2 µg L⁻¹ Sb, were compared in both in-atomizer collection and on-line atomization modes with the 1 mol L⁻¹ HCl matrix used previously.

Foaming in the gas–liquid separator resulting from the reaction between the acid and the reductant was observed when working

with the HAc/HCl mixture; however, the peak areas and peak shapes with on-line atomization mode did not differ from reference measurements. In contrast, when using the HAc/HCl mixture, sensitivity of the collection mode was 22% lower and precision was impaired by a factor of two compared to reference measurements. This is probably due to the spray (resulting from the reaction between acid and reductant) entering the inlet arm of the trap-and-atomizer device and decreasing the trapping efficiency. In order to avoid the spray transport to the device, a PTFE tape was placed over the male standard joint of the connecting piece of the GLS. After that the sensitivity in the collection mode with HAc/HCl mixture increased to reach 100% preconcentration efficiency. Also the precision was improved substantially to 3.1% and 1.7% for HCl and HAc/HCl standards, respectively.

The reductant supply was optimized by varying the NaBH_4 concentration. The experiments were made in on-line atomization mode for both media: 1 mol L^{-1} HCl and HAc/HCl mixture. A plateau of integrated absorbance signals was found in both cases at NaBH_4 concentrations between 0.25% and 1.0%. The sensitivity decreased substantially at lower NaBH_4 concentrations (by one third at NaBH_4 concentration of 0.125%); higher concentrations were not tested. The reductant concentration chosen for the following experiments was the same as we found in previous work [13], i.e. 0.5% (m/v) of NaBH_4 in 0.4% (m/v) KOH.

3.2. Tin interference in model solutions prepared in diluted HCl

Since tin is the main constituent of the pewter, its interference on Sb determination was of primary concern. Estimates of Sn concentration in various preliminary prepared leachates by the (liquid sample introduction) GF-AAS showed that Sn concentration increases with leaching time up to 200 mg L^{-1} for the maximum leaching time of 24 h. Considering the 1 + 4 dilution of leachates (refer to Section 2.2), Sn concentrations up to 40 mg L^{-1} in the sample solutions had to be taken into account.

According to the literature [8], a pronounced Sn interference in the determination of other hydride forming elements could be expected under experimental arrangement similar to the present one, corresponding to a tolerance limit (i.e. interferent concentration leading to 10% signal depression) around 0.1 mg L^{-1} Sn for on-line atomization in conventional externally heated quartz tube atomizers. It was found recently [19] that the tolerance limit of Sn interference on the Sb signal was below 1 mg L^{-1} even in the case of on-line atomization in the multiatomizer. However, this was observed for batch mode hydride generation and, mainly, for a relatively high carrier gas flow rate of 1 L min^{-1} , i.e. for conditions implying much lower sensitivity compared to that achieved with the present hydride generator and carrier gas flow rate: the peak area characteristic mass reported in Ref. [19] was 100 pg compared to m_0 of 8–10 pg achieved with the present hydride generator and a carrier gas flow rate optimized for the on-line atomization mode, i.e. without the additional H_2 flow [15,16,18,20,21]. Therefore, the extent of Sn interference on Sb signal was investigated using the model solutions (refer to Section 2.2).

As shown in Fig. 2, the current experimental arrangement in the on-line atomization mode can tolerate Sn concentrations up to 0.2 mg L^{-1} but 20 mg L^{-1} completely suppresses the analyte signal. Generally, in the absence of any collection, i.e. in the case of on-line atomization (assuming also direct transfer mode of hydride generation), the extent of the interference is controlled by the interferent concentration. Consequently, sample dilution could solve the problem [6,11]. However, sensitivity is reduced accordingly in the on-line atomization mode. To get rid of the interference of 40 mg L^{-1} Sn, the measured sample solution would have to be diluted 200 times. Taking into account that the LOD in the on-line atomization mode with the present arrangement would be around

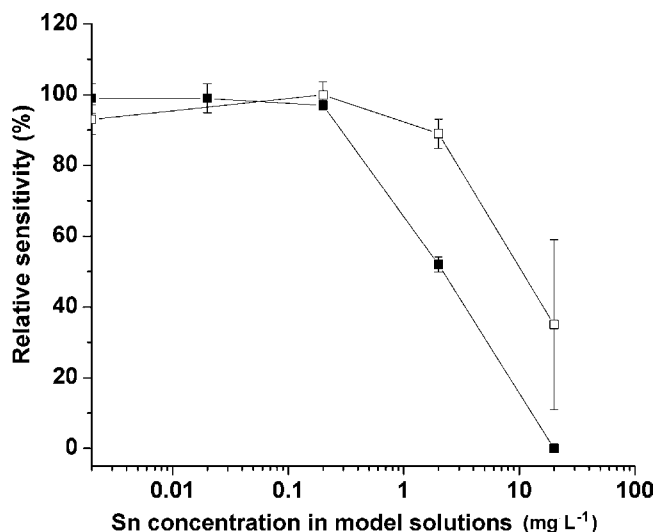


Fig. 2. Tin interference in low acidity (0.1 mol L^{-1} HAc and 0.8 mol L^{-1} HCl) model solutions for on-line atomization (—■—) and collection (—□—) modes; the observed sensitivity is related to the reference sensitivity (see Section 3.1).

0.1–0.2 $\mu\text{g L}^{-1}$ [8,19,20], the corresponding LOD for the sample solution would be unacceptably high: 20–40 $\mu\text{g L}^{-1}$. Obviously, the on-line atomization mode, even when using multiatomizer, cannot handle the interference of the actual Sn concentrations.

Fig. 2 shows also that the resistance to the interference is considerably better in the collection mode, with a tolerance limit around 2 mg L^{-1} . It should be noticed that the shown resistance towards Sn interference is slightly better compared to that we previously found in the case of in-atomizer collection in a conventional externally heated quartz tube atomizer [21]. The additional advantage of the collection mode is potentially much better LOD: for example, a LOD of 13 ng L^{-1} was reported previously [13] for the same experimental parameters as employed in the present work. In the case of an alternative in-atomizer collection technique, i.e. hydride collection at a W-coil, placed in the inlet arm of a T-shaped unheated quartz tube, Sn interference was more pronounced – the tolerance limit was around 0.1 mg L^{-1} [22].

However, even in the collection mode, Sn concentrations expected in the measured sample solutions (up to 40 mg L^{-1}) would exhibit unacceptable signal suppression. In addition, there were significant memory interference effects observed in both atomization modes when working with high Sn concentrations: signals measured after solutions containing high Sn concentrations were lower than when measured after blanks or standards. For example, a decrease of 27% related to the reference signal was observed in the in-atomizer collection mode, when the standard followed a measurement of a model solution containing 20 mg L^{-1} of Sn. Even more serious interference (signal decrease of 36%) was observed in the on-line atomization mode. Similarly, a gradual decrease of observed signals occurred when measuring replicates of the model solution containing 20 mg L^{-1} of Sn. This was responsible for the extremely high standard deviation of the corresponding measurements (see Fig. 2). Also, measured solutions containing high Sn concentrations exhibited a different peak shape compared to standard solutions. In all cases, the original signal was restored only after cleaning the atomizer in the mixture of HNO_3 and HF (refer to Section 2.3). An analogous memory interference effect in Sb measurements due to Sn using on-line atomization in multiatomizer was reported by Flores et al. [19]. The authors suggested that the interference mechanism was a stibine loss on the inlet arm surface modified by the decomposed Sn hydride.

3.3. Mechanism of tin interference

In order to find a way to control the interference, it is desirable to understand its mechanism. In the case of in-atomizer collection mode, interferences can, in principle, occur during generation step and/or during volatilization/atomization step. Interferences occurring during generation step can take place either in the generator (the transport tubings according to definition [6] belongs to the generator) or in the atomizer (trapping interference, see below). The extent of the interferences taking place in the generator does not depend on the analyte concentration but only on the interferent concentration [6]. Consequently, interference extent can be reduced by sample dilution. Interferences occurring during volatilization/atomization take place only in the atomizer. In summary, interferences taking place in the atomizer can occur either during generation step (they will be further termed trapping interferences) or during volatilization/atomization step. The obvious mechanism of trapping interference is a reduction of the trapping capacity of the atomizer surface [8,21]. We have shown previously that the mechanism of interference on Sb in the volatilization/atomization stages was the decrease of atomization efficiency and that, under optimized volatilization conditions, there was no volatilization interference [13,21]. Therefore, interferences taking place in the atomizer during volatilization/atomization stages will be further termed atomization interferences. In essence, the extent of interferences taking place in the atomizer (either trapping interference or atomization interference) can be controlled either by interferent concentration and/or (depending on the actual mechanism of the interference) interferent mass trapped in the atomizer.

Even though the above-reported memory interference takes place in the atomizer, a parallel interference taking place in the generator could not be ruled out without further indications. To get some evidence on interference mechanism, the effect of dilution of model solution containing Sn interferent was tested by comparing peak areas observed in the collection mode for the following measurements: (i) standard solution (i.e. without any Sn added) containing $2 \mu\text{g L}^{-1}$ Sb with 30 s introduction time in the trapping step; (ii) model solution containing $2 \mu\text{g L}^{-1}$ Sb and 20 mg L^{-1} Sn also with 30 s introduction time (this measurement was done under the same conditions as that shown in Fig. 2 for collection mode with 20 mg L^{-1} Sn); (iii) standard solution with $0.2 \mu\text{g L}^{-1}$ Sb with 300 s introduction time; and (iv) model solution containing $0.2 \mu\text{g L}^{-1}$ Sb and 2 mg L^{-1} Sn also with 300 s introduction time. In summary, the same analyte mass of 4 ng was introduced to the hydride generator in all the measurements; the same interferent mass of 40 μg was introduced in measurements (ii) and (iv); no interferent was present in measurements (i) and (iii). Measurement (i) served as a reference – peak areas observed in measurements (ii), (iii) and (iv) were related to those found in measurement (i). The relative peak area of $94 \pm 3\%$ found in measurement (iii) proved that the efficiency of hydride generation, transport, collection and atomization did not change considerably when diluting the sample solution 10 times. The relative peak area observed in measurement (ii) was $45 \pm 4\%$. This agreed well with the analogous measurement (collection mode with 20 mg L^{-1} Sn) shown in Fig. 2. Measurement (iv) yielded the value $56 \pm 4\%$. If the interference took place exclusively in the generator, measurement (iv) should result in the same signal suppression as shown in Fig. 2 for 2 mg L^{-1} Sn (in the collection mode), i.e. the relative peak area should be around 90%. This clear discrepancy verifies that the observed interference takes place prevalently in the atomizer.

The above mentioned better resistance towards Sn interference compared to that previously found in the case of in-atomizer collection in conventional externally heated quartz tube atomizer [21] indicates that the interference observed in the atomizer should be,

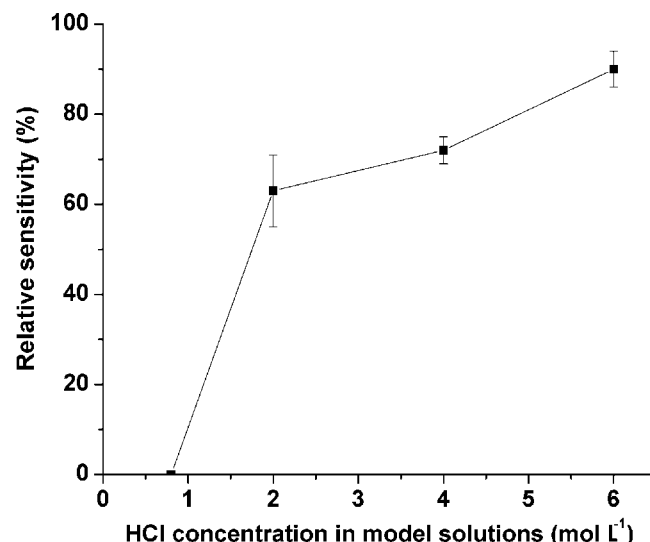


Fig. 3. Influence of HCl concentration on interference of 20 mg L^{-1} tin in the on-line atomization mode; the observed sensitivity is related to the reference sensitivity (see Section 3.1).

at least partially, accounted to an atomization interference. The reason is that the multiatomizer should exhibit better resistance to atomization interferences than the externally heated quartz tube atomizers. The other way round, if the interference observed were the trapping interference, its extent should be lower in the externally heated quartz tube atomizer because of its higher surface area [21]. Moreover, even in the trap-and-atomizer device the capacity of the inlet arm itself seems to be high enough as proved earlier by radiotracer experiments [14]. The trap was proven to retain up to $2 \mu\text{g}$ of Sb (the highest amount studied) as analyte without any change in trapping efficiency. Since also the spatial distribution of trapped analyte, which was focused in a narrow zone in the vicinity of the oxygen delivery capillary, remained the same it can be assumed that the trap capacity is even higher. Thus, the trapping interference appears to be less probable than the atomization one, although there are no experimental data available regarding Sn trapping and volatilization in quartz traps.

However, a stibine loss on the inlet arm surface modified by the decomposed Sn hydride should be also taken into account, since this mechanism is compatible with the memory interference effects observed when working with high Sn concentrations (see above). In summary, even though the measurements performed do not allow to decide conclusively between trapping and atomization interference mechanism, they clearly indicate that to control the interference, stannane had to be prevented to enter the atomizer.

3.4. Tin interference in model solutions prepared in 6 mol L^{-1} HCl

The most straightforward way to prevent stannane to enter the atomizer is to reduce stannane generation efficiency. As shown previously, efficiency of stannane generation decreases with increasing acid concentration [6,23]. Fig. 3 shows the influence of HCl concentration on interference extent of 20 mg L^{-1} Sn in the on-line atomization mode. The signal suppression decreased from 100% to $14 \pm 3\%$, an acceptable range, when the HCl concentration was increased from 0.8 to 6 mol L^{-1} . In the collection mode, the model solution prepared in 6 mol L^{-1} HCl exhibited virtually the same signal suppression. Moreover, the memory interference observed as a consequence of working with high Sn concentrations in 0.8 mol L^{-1} HCl (which could be removed only after cleaning the atomizer in a mixture of HNO_3 and HF – see above) completely disappeared. It should be highlighted that sensitivity observed for the

Table 1
Antimony determination.

Leachate		Sample solution			Leachate
Type of the cup	Leaching time (h)	Dilution ratio	Sn conc. ^a (mg L ⁻¹)	Relative slope ^b	Sb conc. ^c (μg L ⁻¹)
With solder	24	20	5.0	0.73 ± 0.07	10.0 ± 0.7
With solder	12	10	10	0.61 ± 0.07	7.6 ± 1.1
With solder	3	10	2.0	0.60 ± 0.06	2.7 ± 0.1
With solder	1	5	0.15	0.95 ± 0.06	0.180 ± 0.003 ^d
Without solder	24	60	0.8	0.79 ± 0.06	38.0 ± 2.5
Without solder	12	20	8	0.83 ± 0.07	6.3 ± 0.7
Without solder	3	5	3	0.57 ± 0.03	1.00 ± 0.04
Without solder	1	5	0.03	^e	^e

^a Concentration in the measured sample. Estimated by GF AAS. Uncertainty 20%.^b Slope of the calibration function in the sample solution related to that in standards prepared in the mixture of 0.1 mol L⁻¹ HAc and 6 mol L⁻¹ HCl.^c Sb concentration in the leachate calculated from Sb concentration in the sample solution determined by the analyte addition technique.^d Since Sb content in the leachate was lower than LOD the introduction time was increased four times to 120 s (corresponding to 8 mL of sample solution).^e Analyte addition technique was not applied for this sample – Sb concentration in the leachate was 4.1 ± 0.26 μg L⁻¹. It was calculated from Sb concentration in the sample solution determined by the external calibration technique.

standard solutions in 6 mol L⁻¹ HCl either in on-line atomization mode or in the in-atomizer collection mode did not differ significantly from the reference measurements (see above). This proves that (i) efficiency of hydride generation in model solutions prepared in 6 mol L⁻¹ HCl is the same as in 1 mol L⁻¹ HCl and (ii) preconcentration efficiency in model solutions prepared in 6 mol L⁻¹ HCl is 100%.

A higher acid concentration could be expected to reduce Sn interference extent even more, however, for the sake of experimental comfort, 6 mol L⁻¹ HCl was chosen as a compromise for further work. Decreasing Sn concentration from 20 to 10 mg L⁻¹ resulted in an interference-free measurement: the peak area observed in the collection mode did not significantly differ from that for an Sb standard. Consequently, Sn tolerance limit (6 mol L⁻¹ HCl, collection mode) was between 10 and 20 mg L⁻¹.

In order to find the nature of the interference observed in the model solution prepared in 6 mol L⁻¹ HCl, stibine and stannane were generated and trapped separately from the standard solution containing 2 μg L⁻¹ Sb and from the model solution containing 20 mg L⁻¹ Sn prepared without Sb (both solutions prepared in 6 mol L⁻¹ HCl): first stibine followed by stannane and vice versa. Peak areas observed in the collection mode for the following measurements were compared: (i) the standard solution measured in the conventional way; (ii) standard solution followed by the model solution; and (iii) model solution followed by the standard solution. Measurement (i) served as a reference – peak areas observed in measurements (ii) and (iii) were related to those found in measurement (i). The relative peak areas of 82 ± 4% and 90 ± 5%, respectively, were observed in measurements (ii) and (iii). They did not significantly differ from that for the conventional generation of the corresponding model solution containing 20 mg L⁻¹ Sn and 2 μg L⁻¹ Sb in 6 mol L⁻¹ HCl (see Fig. 3). This suggests that the interference observed in 6 mol L⁻¹ HCl, even though less pronounced than in the case of lower acid concentrations, takes place also in the atomizer. If it took place in the generator, measurements (ii) and (iii) should yield relative peak areas around 100%. The observation that relative peak areas of both measurements did not significantly differ from each other thus indicates, in agreement with the discussion above, that this is an atomization interference rather than a trapping one. If it were the trapping interference, one would expect relative peak areas in measurements (ii) and (iii) close to 100% and equal or lower than shown in Fig. 3 (86 ± 2%), respectively. It means that the observed interference is due to interferent trapped and volatilized, at least partially, at the same time with the analyte.

3.5. Figures of merit

The figures of merit were determined for an Sb solution prepared in 6 mol L⁻¹ HCl + 0.1 mol L⁻¹ HAc using the in-atomizer

collection mode (30 s introduction time, 2 mL of solution). The sensitivity, expressed as m_0 , was found to be 20 pg, which agrees reasonably well with the previously reported value of 25 pg [13], obtained with the same trap-and-atomizer device. The calibration graph was linear up to an analyte mass of 2 ng (corresponding to analyte concentration of 1 μg mL⁻¹). The peak area sensitivity decreased by around 10% at the concentration of 2 μg L⁻¹ (corresponding to an analyte mass of 4 ng). This should be accounted to the effect of non-absorbable radiation since the typical peak height for the concentration of 2 μg L⁻¹ Sb was around 1.5 absorbance. The repeatability at the concentration level of 1 μg mL⁻¹ was 1.6% (RSD). The LOD estimated from the standard deviation of 10 blank measurements was 0.03 μg L⁻¹. This is about two times higher compared to our previous measurements [13]. It should be accounted to contamination of the employed HAc – the typical Sb concentration in blank was around 0.1 μg L⁻¹. The LOD could probably be improved by increasing the solution volume of 2 mL, however, this was not tested because of the above discussed Sn interference; the atomization interference would be more serious when using measured greater solution volume.

The LOD observed for the collection mode was almost one order of magnitude better compared to that roughly estimated for on-line atomization mode (employing solutions prepared in 6 mol L⁻¹ HCl + 0.1 mol L⁻¹ HAc).

3.6. Antimony determination in sample solutions

Because of the limited volume of leachates that was available they had to be diluted. The lowest employed dilution was 5 times. Dilution inevitably impaired the LOD for the leachates, e.g. 5 times dilution corresponds to an “effective” LOD of 0.15 μg L⁻¹. However, higher leachate dilution might be necessary, depending on the analyte concentration in leachates because of increasing calibration graph curvature at Sb concentrations above 1.5 μg L⁻¹ (refer to Section 3.5). To estimate optimal dilution of individual leachates, all samples were first diluted five times, and then diluted further if necessary as a compromise between effective LOD, linear response and resistance towards interferences.

Calibration functions, prepared by the analyte addition technique, were checked in sample solutions made from various leachates. Typically, the slope of the calibration function was significantly lower compared to that for standard solutions even though Sn concentration in the sample solutions should be lower than the tolerance limit specified in Section 3.4. Regarding the linearity of the calibration functions, no curvature was observed for Sb concentrations lower than 1.5 μg L⁻¹. Therefore, the analyte addition technique was used for Sb determination in all sample solutions; the results are shown in Table 1.

Even though the aim of this work was not to investigate in detail the migration of Sb from the cup material to the leaching solution or the influence of the solder on the metal migration, some preliminary conclusion can be drawn. In general, analyte content in leachates increases with the leaching time. There is no correlation between Sb content in the leachates and the type of cup (with or without solder). Sb concentrations in the samples leached for 1 and 3 h (between 0.18 and 4.1 $\mu\text{g L}^{-1}$) are below the established safe limits for drinking water specified by Commission of the European Communities (5 $\mu\text{g L}^{-1}$) [24] or by Brazilian legislation (6 $\mu\text{g L}^{-1}$) [25]. In contrast, leachates obtained after 12 and 24 h contain concentrations above these limits.

3.7. Interferences observed in sample solutions

It should be highlighted that the slopes of calibration functions for essentially all samples were significantly lower than slopes obtained for standards (Table 1). This indicates an interference occurring in all measured samples. The interference cannot be straightforwardly accounted to Sn since its concentration in the majority of the sample solutions (Table 1) is well below the Sn tolerance limit (refer to Section 3.4). An analogous argument holds for other hydride forming elements since their concentration in pewter, and consequently in leachates, should be much lower than their tolerance limits for in-atomizer collection in a quartz tube atomizer [21]. To get some evidence on the mechanism of the observed interference, analogous experiments as those described in Section 3.3 were made. The effect of dilution of leachates obtained for the cup with solder at leaching times of 3 and 24 h was tested by comparing peak areas observed in the collection mode for two measurements: (i) a “conventional” measurement based on 30 s of introduction time of the sample solutions using 10-fold and 20-fold dilution, respectively, as shown in Table 1 and (ii) a measurement based on ten times longer (300 s) introduction time of the sample solutions prepared using ten times higher dilution, i.e. a dilution ratio of 100 and 200, respectively. The peak areas observed in measurements (i) and (ii) were (within the experimental uncertainty of 5%) the same for both leachates. This is a proof that the interference observed takes place in the atomizer. The arguments are analogous as those discussed in Section 3.3 in the case of Sn interference in model solutions. It can be concluded, that the source of interference is an unknown volatile compound transported to the atomizer together with stibine.

Tentative measurements indicated that the interference was more serious in the on-line atomization mode; for example, the relative sensitivity of 10 times diluted 24 h leachate of the cup with solder was 38% in contrast to the relative sensitivity of 59% obtained for the same sample solution in the case of the collection mode. This is, besides the above specified much better LOD, another argument to prefer the collection mode over the on-line atomization mode.

4. Conclusions

The aim of this work was to demonstrate usefulness of the hydride generation in-atomizer collection for the determination

of Sb in matrices containing extremely high concentrations of another hydride forming element. Therefore only a limited number of determinations was made, which does not allow to draw final conclusions regarding exact Sb concentration versus leaching time in leachates from various types of pewter utensils. Nevertheless, it can be concluded that storage of vinegar-like solutions in pewter cups for more than 3 h is not safe in terms of Sb content.

It is believed that the present method can be used as a tool for a detailed investigation of the migration of Sb from the cup material to the leaching solution and of the influence of the solder on the metal migration.

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