



Electrochemical hydride generation of thallium

M.H. Arbab-Zavar^{a,*}, M. Chamsaz^a, A. Yousefi^b, N. Ashraf^a

^a Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

^b Pare-Taavous Research Institute, Mashhad, Iran

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ABSTRACT

An electrochemical hydride generation (ECHG) technique was developed to improve the determination of thallium by atomic spectrometry. The technique is based on the catholyte variation system for production of thallium hydride. Using Pb–Sn alloy as cathode, a transient peak shaped signal was achieved and its height, the maximum absorbance value, was taken as an analytical parameter. Parameters that might affect the hydride generation efficiency were investigated and the analytical performance of the method under the optimized experimental conditions was assessed. The linear range was 1–250 ng mL⁻¹ for thallium and the relative standard deviation of the method was 4.2% (RSD, $n = 7$). The LOD for thallium was found to be 0.8 ng mL⁻¹, showing a significant improvement relative to conventional chemical hydride generation techniques. The proposed method was applied to the determination of thallium in unalloyed zinc standard reference material. This method offers high sensitivity, simplicity, rapidness, freedom from reagent and low acid consumption.

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1. Introduction

Thallium has been found to be an environmentally hazardous element because of its toxic effects. This metal is introduced into the environment mainly as the waste product of zinc, cadmium, and lead industries and also results from the combustion of coal. It is regarded as one of the most toxic heavy metals causing both chronic and acute poisoning [1]. It is, therefore, important to detect and determine thallium in a wide range of matrices, i.e. environmental, biological, clinical, geological, and metallurgical samples. Since the total concentration of thallium is generally very low, an analytical technique with high sensitivity and low detection limit is required. There are several analytical techniques available for determination of thallium, i.e. spectrophotometry and fluorimetry, atomic absorption and fluorescence spectrometry, inductively coupled plasma and isotope dilution mass spectrometry, potentiometry and voltammetry, and nuclear techniques [2,3]. Among these, stripping voltammetry has received the most attention owing to its high sensitivity and ability to detect the redox species of metals. However, analysis of thallium by this method suffers from interferences by other metals especially cadmium [4]. Although flame atomic absorption spectrometry (FAAS) is a simple and easily available technique, its application is restricted due to lack of sensitivity for trace determinations of thallium.

Vapour generation techniques in combination with atomic absorption spectrometric determination (AAS) are sensitive analytical methods. These techniques offer several advantages relative to conventional nebulization methods, which include improved selectivity, elimination of nebulizer, analyte preconcentration, and more efficient analyte atomization [5–8]. However, reports on thallium vapour generation are few [9–14]. Thallium vapour generation, presumably as hydride, was first reported by Yan et al. [9]. The method was less sensitive than conventional FAAS, as well as being subjected to large positive interferences from the presence of other hydride-forming elements. Ever since, many attempts have been made to improve its sensitivity. These include applying continuous flow methodologies [10], in situ trapping of hydrides in a graphite tube along with electrothermal AAS determination [11], using palladium and rhodamine B as enhancement reagent in flow injection hydride generation AAS [12], and employing an integrated atom trap atomizer in hydride generation AAS [13]. Although the application of trapping techniques somewhat improves the limit of detection, the efficiency of hydride generation is still low.

Electrochemical hydride generation (ECHG) proved to be a suitable alternative to conventional chemical hydride generation due to several advantages. The most significant advantages include elimination of NaBH₄ (an expensive unstable substance, and also a source of contamination), similar reaction media for all hydride-forming elements, better tolerance of interferences, better reproducibility, higher sensitivity, and independence from analyte oxidation state when using cathode materials with high hydrogen overvoltage [15]. As far as our review shows, there is no report on electrochemical hydride generation of thallium. In the present research, effort

* Corresponding author. Tel.: +98 511 8797022; fax: +98 511 8796416.
E-mail address: arbab@um.ac.ir (M.H. Arbab-Zavar).

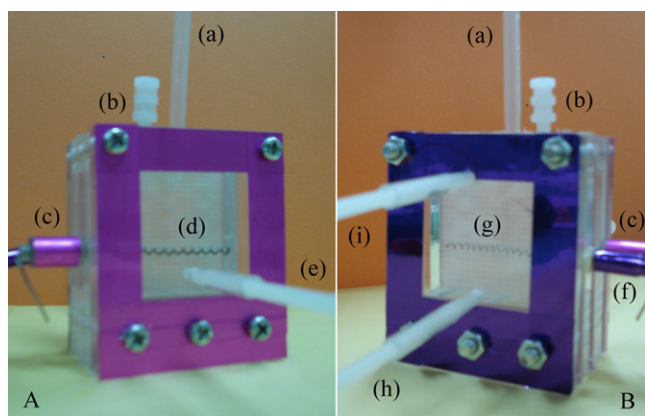


Fig. 1. Electrochemical hydride generation cell. Cathodic (A) and anodic (B) compartments: connection to quartz tube atomizer (a); sample inlet (b); cathode holder (c); helix shaped Pb–Sn cathode (d); carrier gas entry (e); anode holder (f); helix shaped Pt anode (g); anolyte inlet (h); anolyte outlet (i).

has been made to develop a technique for electrochemical hydride generation of thallium. Using catholyte variation system [16,17], a transient peak shaped signal was obtained and its height, the maximum absorbance value, was measured as an analytical parameter. Accordingly, this technique resulted in improvement on thallium hydride generation. A mechanism for electrochemical generation of thallium hydride is proposed. Effective and operative parameters on the obtained signal were optimized. Analytical performance of the method was compared to the previously reported chemical hydride generations of thallium.

2. Experimental

2.1. Instrumentation

A Shimadzu 680 atomic spectrometer (Shimadzu, Japan) equipped with an electrically heated quartz tube atomizer (150 mm length, 4.2 mm inner diameter) operated at 1000 °C was used for atomic absorption measurements. Thallium hollow cathode lamp (Hamatsu Photonics, Japan) operated at 3 mA was employed as radiation source. The spectral bandwidth was set at 0.5 nm and absorbance was measured at 276.8 nm.

2.2. Electrochemical hydride generation system

Various views of the batch electrolytic hydride generator are shown in Fig. 1. Electrochemical hydride generator consists of two compartments; batch cathodic (Fig. 1A and continuous anodic (Fig. 1B) chambers separated by a nafion membrane (Dupont, USA) and has been described in details in the previous publications [16,17].

A programmable power supply (Promax FA-851, Spain, maximum current of 2 A and maximum voltage of 32 V) operating at constant current and voltage modes is connected to the electrochemical cell.

2.2.1. Cathodic compartment

Carrier gas (Argon, 99.999% pure) entry is placed at the bottom of the cathodic compartment. This design facilitates the separation of gaseous products from the cathode surface and aqueous solution. The gaseous reaction products; hydrides and hydrogen formed at the cathode, are separated from aqueous solution, and directed to the electrically heated quartz tube by the carrier gas stream via a connecting tube (PVC, length of 20 cm, 3 mm i.d.) and determined under the operating conditions by AAS. As the cathodic materials,

lead, tin, lead–tin (Pb–Sn 37:67, Asahi solder, Singapore, 0.8 mm diameter), graphite, tungsten wire (99.98% pure, AESAR, Johnson Matthey Inc., 0.5 mm diameter), dental amalgam (32% Ag, 14.7% Sn, 6.7% Cu and 46.7% Hg amalgam, coltèn whaledent®, USA), platinum (Merck), and silver wire have been investigated. After the termination of a run process, a peristaltic pump drains off the contents of the cathodic compartment.

2.2.2. Anodic compartment

A platinum coil (surface area of 1 cm²) serves as the anode. The anolyte is circulated by a multiple channel peristaltic pump (Gilson, Minipuls 3, ANACHEM) to remove oxygen from the anodic compartment. The circulated anolyte needs only to be changed after 40 h of operation.

2.3. Data acquisition and transformation

The transient signals were recorded using a graphical printer (PR-5) equipped with a monitor and transformed to digital data using an in-house software (Graph-7).

2.4. Procedure

Initially, the electrochemical hydride generation cell was connected to quartz tube atomizer via PVC tubing. Then, the circulation of the anolyte (0.5 mol L⁻¹ Na₂CO₃) was started and the flow rate of the carrier gas adjusted. In each regular measuring cycle, the electrode (cathode) was placed into its position and connected to power supply. The acidified thallium solution (catholyte solution containing anolyte) was then introduced and measurement performed by applying an appropriate voltage to the cell (between the cathode and the anode). The gaseous electroreaction products were transported to the quartz tube atomizer by the carrier gas stream and the transient signal was measured. The transient signal was peak shaped and its maximum absorbance value was measured as an analytical parameter.

2.5. Reagents and materials

All chemicals were of analytical grade except cited otherwise. Standard solution (1000 µg mL⁻¹) of Tl(I) was prepared by dissolving the proper amounts of thallium(I) nitrate (Prolab) in dilute nitric acid solution. Solutions of 1 mol L⁻¹ of HCl, HNO₃ and H₂SO₄ were prepared by diluting analytical grade concentrated acids. Working solutions were prepared by mixing the proper amounts of Tl standard solutions and 1 mol L⁻¹ sulfuric acid solution and diluting to desired volume.

2.6. Reference material

Validation of the method described in this work was carried out using certified unalloyed zinc reference material. The European Reference Material ERM[®]-EB325 was purchased from the Institute for reference materials and measurement (IRMM).

2.7. Sample preparation

Exactly, 1 g of the solid reference material was weighted, transferred to a 50 mL Erlenmeyer flask, and 5 mL of concentrated nitric acid was then added. After complete dissolution of the solid sample, the remaining solution was evaporated at the temperature of 80 °C to approximately 0.5 mL final volume. Then, 50 mL of deionized water and 3.3 g of ammonium carbonate were added, respectively. After 30 min, the mixture was filtered through a glass filter, transferred to a 200 mL calibrated flask, and diluted to volume with

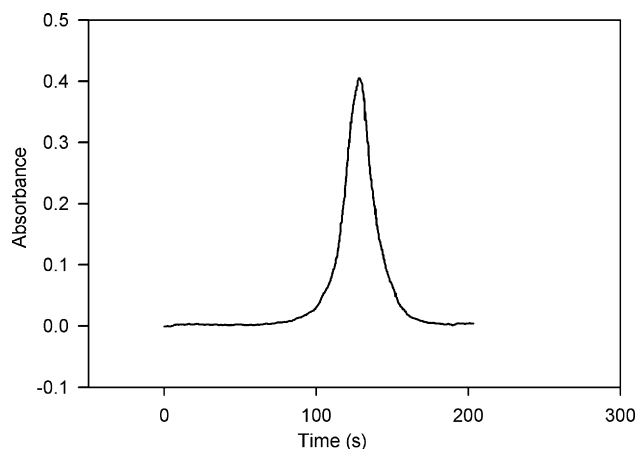


Fig. 2. Transient peak shaped signal resulted from electrochemical hydride generation of thallium (200 ng mL^{-1}) under optimized condition.

deionized water. Prior to the analysis, appropriate dilutions were performed depending on the concentration level of the thallium.

3. Results and discussion

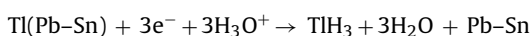
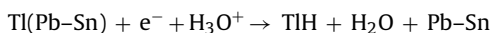
3.1. Generation of thallium hydride species

Catholyte variation electrochemical system was applied to generate thallium hydride species. The method has been described in details in previous publications [16,17]. During electrolysis, the hydronium ions and water are gradually reduced to hydrogen molecules. Meanwhile, sodium ions are diffused from anodic chamber through the nafion membrane and the pH is increased during the electrolysis due to low concentration of hydronium ions. The peak shaped transient signal (Fig. 2) produced during electrolysis process is observable at neutral to moderately basic pH values.

To account for the mechanism of thallium hydride generation, the initial reaction is considered to be the electrodeposition of Tl ions at the surface of Pb–Sn cathode [1,2]. By considering the values of standard potential: $\text{Tl}^{3+} + 2\text{e}^- \rightarrow \text{Tl}^+$; $+1.25 \text{ V}$, $\text{Tl}^{3+} + 3\text{e}^- \rightarrow \text{Tl}$; $+0.92 \text{ V}$ and $\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}$; -0.34 V , deposition of both Tl^+ and Tl^{3+} would occur at the electrode surface, at highly negative working potentials employed. High hydrogen overvoltage, negative working potentials, and high electrolytic currents facilitate this process:



Pb–Sn alloy used as the cathode material involves sp-metals with filled d-orbital, so low hydrogen adsorbing power and high hydrogen overvoltage is expected [24]. This hypothesis is supported by our previous experiments showing high hydrogen overvoltage for Pb–Sn alloy relative to Pt, graphite, Sn and Pb [17]. Therefore, the following electrochemical mechanism is proposed for thallium hydride formation [24]:



The real identity of the generated species is unknown. When quartz tube atomizer was in the room temperature, no signal was observed. By raising the temperature, the signal was gradually increased. This observation ensures that the generated vapours are in the molecular form.

There have been many studies considering the stability of thallium hydride species, i.e., TIH , TIH_2 , TIH_3 , TI_2H_2 , TI_2H_2 and $\text{Tl}^+(\text{H}_2)_n$

Table 1
Optimized operating condition.

Operating parameter	Optimized value
Anolyte concentration (mol L^{-1})	0.5
Anolyte flow rate (mL min^{-1})	6
Sample volume (mL)	13
Catholyte concentration (mol L^{-1})	0.003
Carrier gas flow rate (mL min^{-1})	100
Atomizer temperature ($^\circ\text{C}$)	1000
Cathode surface area (cm^2)	1.75
Applied voltage (V)	20

[18–23]. The monovalent Group 13 hydrides have been all detected in the gas phase and their spectroscopic properties are currently known [21].

3.2. Optimization of operating parameters

The influence of fundamental operating parameters, primarily the cathode material, catholyte and anolyte types, electrolytic current and potential, cathode surface area, atomizing temperature, and concentration of the anolyte and catholyte was thoroughly studied and will be discussed later. The optimized values for operating conditions have been shown in Table 1.

3.2.1. Cathode material

Lead, tin, Pb–Sn alloy, tungsten, platinum, silver, dental amalgam, and graphite rod were examined as the cathodic materials. With sulfuric acid (0.003 mol L^{-1}) as the catholyte solution, the signals generated using all cathodic materials were negligible except those from tin and Pb–Sn. Tungsten, platinum, silver, and graphite rod were not able to produce any detectable thallium hydride signal, probably because of their low hydrogen overvoltages. In the case of dental amalgam, thallium was deposited at the surface of the electrode as amalgam and no detectable signal was produced. Despite of high hydrogen overvoltage values reported for lead [17,24], no signal was produced and by applying higher voltages, complete deterioration of the electrode was observed. Tin and Pb–Sn alloy generated transient peak shaped signals with greater sensitivity for Pb–Sn alloy. High hydrogen overvoltage [17] and microcrystalline structure of Pb–Sn alloy were supposed to be responsible for the higher efficiency. Based on these observations, Pb–Sn alloy was preferred as the cathodic material and used for the rest of the experiments.

3.2.2. Catholyte and anolyte electrolyte solutions

Supporting electrolyte is necessary to provide electric conductivity. So, dilute solutions (0.01 mol L^{-1}) of HCl, H_2SO_4 and HNO_3 were examined as catholyte solutions. Generation of hydrides took place in all acidic media. The signals attained with nitric and hydrochloric acids were not considerably different; where in the case of sulfuric acid, the generated signal was of higher intensity. Therefore, sulfuric acid was selected as catholyte supporting solution for further experiments. Precipitation and complex formation between Tl^+ and chloride ions in hydrochloric acid [25] and oxidizing properties of NO_3^- in nitric acid decrease the tendency of thallium ions for reduction and deposition at the electrode surface. Based on the proposed mechanism, this results in the reduction of hydride generation efficiency.

As anolyte solutions, equimolar solutions of Na_2CO_3 , Na_2SO_4 , NaCl , KNO_3 and H_2SO_4 were tested. Except for H_2SO_4 , all electrolytes produced similar signals. When H_2SO_4 was used, the system was not able to produce any detectable signal. This is in accordance with the proposed mechanism. Based on the catholyte variation mechanism, pH plays an essential role in the generation of hydrides. The pH of the solution would be adjusted from acidic to

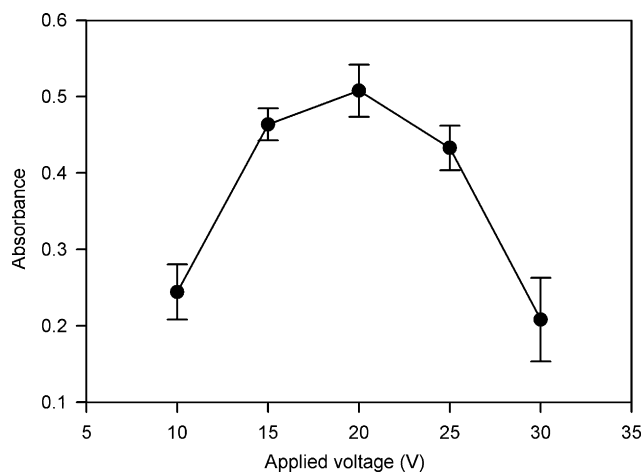


Fig. 3. Effect of the applied voltage on thallium hydride signal.

basic by two major phenomena: first, consumption of hydronium ions during electrolysis and second, their transport through the nafion membrane. In the case of Na_2CO_3 , Na_2SO_4 , NaCl , and KNO_3 , hydronium ions diffuse from cathodic chamber through nafion membrane while Na^+ ions enter from the anodic chamber. This process decreases the concentration of hydronium ions and thus increases the pH of the solution. In the case of H_2SO_4 as anolyte solution, although the hydronium ions are consumed during electrolysis process, more hydronium ions diffuse from anodic chamber due to much higher concentration of sulfuric acid (about 150 times). This process will prevent any pH variation; therefore, the suitable pHs for evolution of hydrides would never be reached. Na_2CO_3 solution was selected because of its inertness and higher conductance for pH dependent membrane.

3.2.3. Designating electrolysis working mode

Most of the electrochemical hydride generation systems utilize high catholyte concentrations ($1\text{--}3\text{ mol L}^{-1}$). In such systems, constant current and constant voltage modes are not distinguishable. In fact, constant currents lead to constant voltages during electrolysis process and vice versa. The main difference of the present system (catholyte variation) lies in this point. In the present system, the concentration of catholyte is lowered to approximately 1%. Therefore, the composition of the catholyte as well as the concentration of the ions and the ionic conductance in the cathodic chamber vary during electrolysis process. At these conditions, two working modes are possible: constant current and constant voltage modes. Both systems were examined to find the most suitable and sensitive working mode.

3.2.3.1. Constant voltage mode. Working voltage is limited by the power supply operation. The maximum voltage attainable by the power supply is 32 V. Generation of hydrides was studied in the range of 0–32 V. As shown in Fig. 3, the most intense signal was attained at 20 V.

3.2.3.2. Constant current mode. High working electrolysis currents are needed to efficiently produce thallium hydride. For each catholyte concentration, the maximum practical current was applied and the signal was recorded. Considering peak height as the analytical parameter, in all cases the intensities were much lower than constant voltage mode. Fig. 4 shows the signals obtained by exerting 125 mA constant current and 20 V constant voltage to a solution of thallium in 0.003 mol L^{-1} of sulfuric acid. As the results show, although the peak area of the signal obtained in the constant current mode is somewhat higher than that obtained by apply-

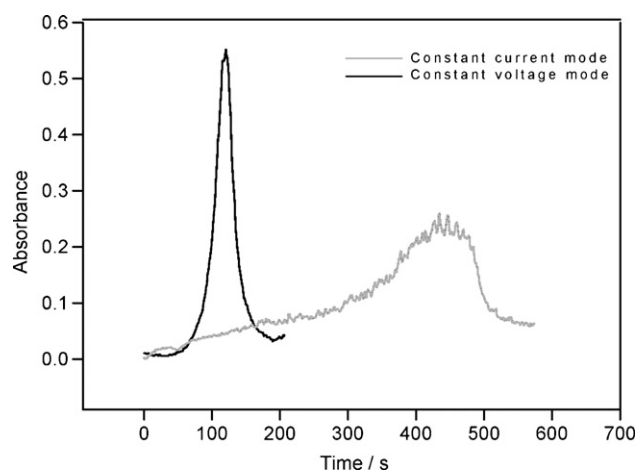


Fig. 4. Comparison between constant current and constant voltage working modes.

ing constant voltage, this peak is broad and noisy while presenting low reproducibility. By contrast, the signal obtained in the constant voltage mode is sharp, symmetrical and reproducible. Moreover, the evolution time in the constant voltage mode is about one-third in comparison to the constant current mode. Thereupon, constant voltage mode (with 20 V) was selected as a suitable working mode. Working in constant current mode is suggested where trapping techniques are used.

3.2.4. Influence of aging of the cathode

Replicate experiments were performed without replacing the old electrode. Results (Fig. 5) show that using the electrode for the second and third consecutive runs will produce only 80% of signal attainable for the first run. By using the electrode in more replicates, the signal gradually declines to 30% in the 12th replicate. This proves that the active sites of the electrode are deteriorated during the electrolysis process, resulting in a change of surface composition. Based on such observations, the Pb–Sn electrode was replaced at the beginning of each experiment to obtain a reproducible signal.

3.2.5. Influence of the cathodic surface area

Enlarging the cathode surface will result in increasing the electrolytic current and the active sites for generation of hydrides; both phenomena elevate the efficiency of hydride generation. Influence of the cathodic surface area on the hydride generation efficiency was investigated over the range of $0.6\text{--}2.0\text{ cm}^2$ as shown in Fig. 6.

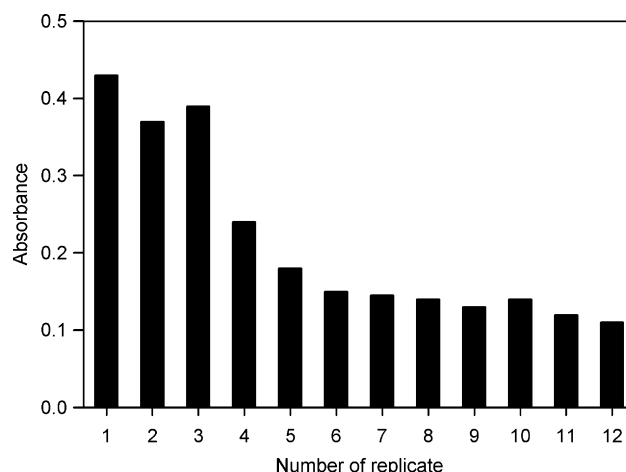


Fig. 5. Influence of the electrode aging on the signal intensity.

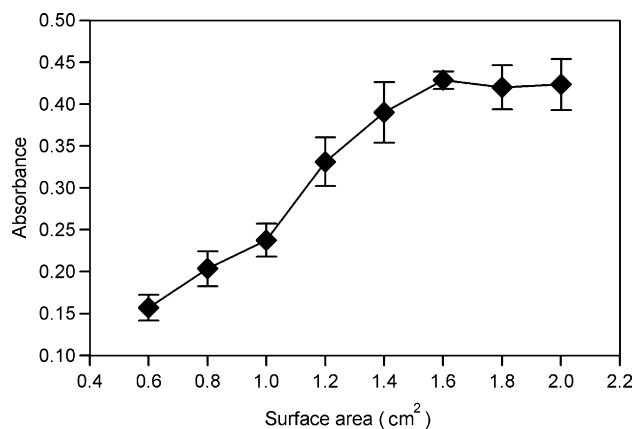


Fig. 6. Optimization of cathode surface area.

Extension of the cathodic surface to 1.5 cm² resulted in a sharp increase in the signal, followed by a distinctive decrease of the slope. In practice, a helix shaped cathode with the surface area of 1.75 cm² was used.

3.2.6. Influence of the anolyte flow rate

The effect of the anolyte flow rate was investigated within 0–7.5 mL min⁻¹ interval. Circulation of the anolyte prevents consuming extra amounts of the anolyte and hence maintaining a constant concentration of the anolyte during the experiment. Also, by circulating the anolyte in the system, the sensitivity and reproducibility would increase. As shown in Fig. 7, the maximum signal intensity was achieved in the range of 3–6 mL min⁻¹ and the sensitivity decreased at higher flow rates. Therefore, the flow rate of 6 mL min⁻¹ was chosen as the optimized parameter.

3.2.7. Influence of sample volume

Increasing the volume of the sample resulted in higher signal intensity. The maximum capacity of the cathodic chamber was 18 mL. However, due to upward flowing of the carrier gas, it was impossible to utilize the entire volume. In practice, sample volumes more than 13 mL would be resulted in liquid blocking of the connecting tube, thus spoiling the sensitivity and reproducibility. Therefore, 13 mL was selected as the optimized practical sample volume.

3.2.8. Influence of the carrier gas flow rate

Carrier gas would be necessary to immediately transfer the generated hydrides at the electrode surface to the quartz tube atomizer.

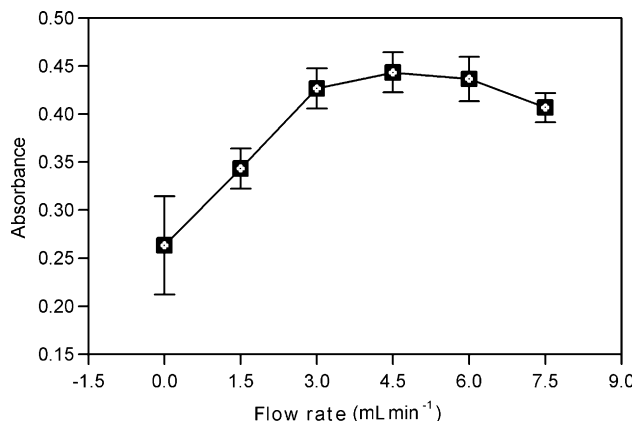


Fig. 7. Optimization of anolyte (Na₂CO₃, 0.5 mol L⁻¹) flow rate.

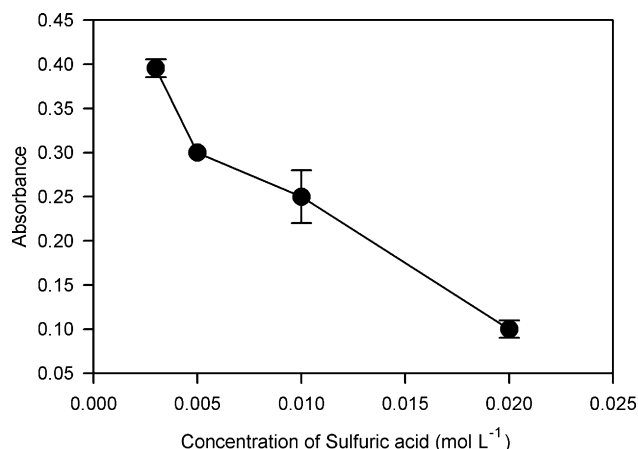


Fig. 8. Optimization of catholyte (sulfuric acid) concentration.

Increasing the flow rate of the carrier gas led to higher sensitivity and lower evolution time for the signal. The flow rate of 100 mL min⁻¹ was selected as an optimized flow rate, since the higher flow rates may result in liquid blocking of the connecting tube and low reproducibility.

3.2.9. Concentration of catholyte

Concentration of hydronium ion varies during the electrolysis process. When the acidic catholyte solution is neutralized, the signal starts to rise. Therefore, it is expected that higher concentrations of catholyte lead to longer evolution times of the signal. However, this would be true if the system was working at constant current mode. In constant voltage mode, employed in this work, concentration of catholyte is also a determining factor on electrolytic current. Increasing the catholyte concentration would lead to higher electrolytic currents and therefore, shorter peak evolution times. In fact, the catholyte concentration affects two compromising factors on the evolution time. Moreover, concentration of catholyte has a significant impact on the sensitivity. With respect to the generation efficiency of the volatile hydrides and the amount of H₂ co-produced in the reaction, the concentration of acid is very critical for the performance of the ECHG. The influence of sulfuric acid concentration as the catholyte was studied within the range of 0.003–0.02 mol L⁻¹. The results show that the lower acidic concentrations produce more sensitive signals, since the peak area and the peak height (Fig. 8) both increased by lowering the acid concentration. The use of the concentrations lower than 0.003 mol L⁻¹ was avoided because of considerable loss of reproducibility and destructive effects on nafion membrane.

3.3. Analytical performance

3.3.1. Analytical figures of merit

The calibration curve was constructed under the optimized conditions (Table 1) within the 1–1000 ng mL⁻¹ concentration interval of thallium and found to be linear in the range of 1–250 ng mL⁻¹. The results of this calibration are listed in Table 2. The sensitivity of

Table 2
Analytical figures of merit for ECHG of Tl.

Parameter	Value
Calibration sensitivity (ng mL ⁻¹)	1.68 × 10 ⁻³
Dynamic range (ng mL ⁻¹)	1–250
Characteristic concentration (ng mL ⁻¹)	1.0
Detection limit (ng mL ⁻¹)	0.8
RSD (%)	4.2

Table 3

Effect of co-existing ion (concentration of $10 \mu\text{g mL}^{-1}$) for determination of 100 ng mL^{-1} Tl.

Species	Recovery (%)
NO_3^-	93
NO_2^-	87
Cl^-	102
$\text{C}_2\text{O}_4^{2-}$	78
PO_4^{3-}	89
Al^{3+}	99
Cu^{2+}	130
Cd^{2+}	78
Zn^{2+}	100
Mn^{2+}	10
Mg^{2+}	0
Co^{2+}	5
Ni^{2+}	0
Pb^{2+}	59
Sn^{2+}	55
Cr^{3+}	0
Hg^{2+}	102

Table 4

Analytical results of thallium for certified reference material.

Sample	Found (mg kg^{-1})	Certified (mg kg^{-1})	Recovery (%)
ERM [®] -EB325	37.0 ± 2.7	36.8 ± 1.2	100.5

the method, as determined from the slope of the calibration graph, is 1.68×10^{-3} absorbance $\text{ng}^{-1} \text{ mL}$. Calculated absolute detection limit based on the variability of the blank ($3s_b$ criterion) for seven measurements is 0.8 ng mL^{-1} . The reproducibility (RSD) for seven replicate measurements at 120 ng mL^{-1} of thallium, was obtained to be 4.2%. A simple comparison of the detection limit with those calculated in the previously existing HG-AAS methods shows a remarkable improvement relative to simple batch chemical hydride generation ($0.6 \mu\text{g mL}^{-1}$) [9], continuous flow methodologies (4 ng mL^{-1}) [10] and flow injection hydride generation-AAS (3.4 ng mL^{-1}) [12]. Also, it is comparable with hydride generation-in situ trapping-AAS (0.4 ng mL^{-1}) [13].

3.3.2. Interferences from metal ions and hydride-forming elements

A wide variety of transition metal ions and other hydride-forming elements are known to interfere with the hydride generation by releasing the volatile hydrides in CHG as well as in ECHG, and thus limit the analytical applicability of both techniques [5,15]. In the present study, the influence of concomitant ions was evaluated by analysis of 100 ng mL^{-1} of thallium in 0.003 mol L^{-1} H_2SO_4 in the presence of $10 \mu\text{g mL}^{-1}$ of foreign ions. The results are shown in Table 3. There are several mechanisms responsible for the interfering effects in electrochemical hydride generation. Interferences of the transition metals such as Ni^{2+} , Co^{2+} , Cr^{3+} , Fe^{3+} and Mn^{2+} have been shown to be a result of modification of the cathode surface by the reduced interferences. Transition metals are deposited on the cathode surface and dispersed over the surface, so that the cathode and thus the hydrogen overvoltage will be altered [26–29]. Since the Pb–Sn alloy is a cathode with high hydrogen overvoltage value, deposition of most of the metal ions will reduce the hydrogen overvoltage, lowering the efficiency of hydride genera-

tion. Although this phenomenon may interpret the results, further investigations are required to provide better understanding of the individual interfering effects. Since there are significant interferences from major constituents of real matrices, standard addition method is recommended for real sample analysis.

3.4. Accuracy of the method

To establish the accuracy of the method, certified unalloyed zinc (ERM[®]-EB325) was analyzed. Using the standard addition technique, a recovery of 100.5% was achieved (Table 4). The concentration of Tl found (37.0 ± 2.7) well agreed with the certified value (36.8 ± 1.2).

4. Conclusion

Catholyte variation electrochemical hydride generation was successfully employed to produce thallium hydride species which are supposed to be thallium(I) hydride. The proposed method overcomes the problems of CHG method for production of thallium hydride. The main advantages of the proposed method over the conventional chemical hydride generation method would be its high sensitivity, simplicity, rapidness, freedom of reagent, cost-effectiveness, low acid consumption and environmental cleanness. Efforts are currently being made to overcome its drawbacks by improving the electrochemical hydride generation technique.

References

- [1] I. Bodek, W. Lyman, W.F. Reehl, D.H. Resebatt, Environmental Inorganic Chemistry, Pergamon Press, New York, 1988.
- [2] A.K. Das, M.L. Millli Dutta, M. Cervera, M. de la Guardia, Microchem. J. 86 (2007) 2.
- [3] A.K. Das, R. Chakraborty, M.L. Cervera, M. de la Guardia, Anal. Bioanal. Chem. 385 (2006) 665.
- [4] J. Zen, J. Wu, Electroanalysis 9 (1997) 302.
- [5] P. Pohl, Trends Anal. Chem. 23 (2004) 21.
- [6] A. Ramesh, P. Riyazuddin, Anal. Sci. 21 (2005) 1401.
- [7] A. D'Ulivo, Spectrochim. Acta: Part B 59 (2004) 793.
- [8] T. Nakahara, Anal. Sci. 21 (2005) 477.
- [9] D. Yan, Z. Yan, G. Cheng, A. Li, Talanta 31 (1984) 133.
- [10] L. Ebdon, P. Goodal, S. Hill, J. Anal. Atom. Spectrom. 10 (1995) 317.
- [11] Y. Liao, G. Chen, D. Yan, A. Li, Z. Ni, Anal. Chim. Acta 360 (1998) 209.
- [12] Z. Daan, X. Shukun, Atom. Spectrom. 21 (2000) 136.
- [13] H. Matusiewicz, M. Krawczyk, J. Braz. Chem. Soc. 18 (2007) 304.
- [14] M. Wei, S. Jiang, J. Anal. Atom. Spectrom. 14 (1999) 1177.
- [15] F. Laborda, E. Bolea, J.R. Castillo, Anal. Bioanal. Chem. 388 (2007) 743.
- [16] M.H. Arbab-Zavar, M. Chamsaz, A. Youssefi, M. Aliakbari, Anal. Chim. Acta 546 (2005) 126.
- [17] M.H. Arbab-Zavar, M. Chamsaz, A. Youssefi, M. Aliakbari, Anal. Chim. Acta 576 (2006) 215.
- [18] E.M. Bulewicz, T.M. Sugden, Trans. Faraday Soc. 54 (1958) 830.
- [19] P. Hunt, P. Schwerdtfeger, Inorg. Chem. 35 (1996) 2085.
- [20] X. Wang, L. Andrews, J. Phys. Chem. A 108 (2004) 3396.
- [21] S. Aldridge, Chem. Rev. 101 (2001) 3305.
- [22] K. Balasubramanian, J.X. Tao, J. Chem. Phys. 94 (1991) 3000.
- [23] P. Schwerdtfeger, P.D.W. Boyd, G.A. Bowmaker, H.G. Mack, H. Oberhammer, J. Am. Chem. Soc. 111 (1989) 15.
- [24] E. Denkhaus, F. Beck, P. Buechler, R. Gerhard, A. Golloch, Fresenius J. Anal. Chem. 370 (2001) 735.
- [25] A.A. Ensaifi, B. Rezaei, Microchem. J. 60 (1998) 75.
- [26] W.W. Ding, R.E. Sturgeon, J. Anal. Atom. Spectrom. 11 (1996) 421.
- [27] E. Bolea, F. Laborda, M.A. Belarra, J.R. Castillo, Spectrochim. Acta: Part B 56 (2001) 2347.
- [28] E. Denkhaus, A. Golloch, X.M. Guo, B. Huang, J. Anal. Atom. Spectrom. 16 (2001) 870.
- [29] E. Bolea, D. Arroyo, G. Cepria, F. Laborda, J.R. Castillo, Spectrochim. Acta: Part B 61 (2006) 96.