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Tin film sensor with on-chip three-electrode configuration for voltammetric determination of trace Tl(I) in strong acidic media

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ABSTRACT

The present work describes the trace analysis of Tl(I) in acidic medium (0.05 mol L^{-1} nitric acid) by square wave anodic stripping voltammetry (SWASV) at a tin film sensor with novel configuration. This "green" electroanalytical device features on-chip metal film electrodes (a Sn-film working electrode, a Ag-film reference electrode and a Pt-film counter electrode), fabricated by sputtering the respective metals on a silicon chip. The effect of preconcentration time, preconcentration potential and SW stripping parameters on the Tl(I) detection was studied in detail. The limit of detection for Tl(I) was 1.1 μg L^{-1}, while the % relative standard deviation at the same sensor was 5.2% at the 10 μg L^{-1} level. Finally, the sensors were successfully applied to the direct determination of Tl(I) in an acidified certified lake water sample.

1. Introduction

Thallium is considered a very toxic metal, causing many disorders in biological systems and present in environmental samples at trace concentrations, and therefore sensitive methods are required for its determination [1]. Several methods, based on spectroscopic techniques, have been developed for the analysis of heavy metal ions, including atomic absorption spectrometry (AAS) [2], inductively coupled atomic emission spectrometry (ICP-AES) [3] and inductively coupled plasma mass spectroscopy (ICP-MS) [4]. However, these require expensive instrumentation, complicated measurement procedures and long analysis times. Electrochemical techniques offer a rapid, simple, sensitive and inexpensive alternative to spectroscopy, especially for on-site assays. Among the different electrochemical techniques, anodic stripping voltammetry (ASV) is widely used for the trace determination of heavy metals, mainly owing to its high sensitivity, simplicity and low cost of instrumentation [5]. Moreover, ASV can be readily combined with sensors fabricated using microengineering technologies, thus extending the scope of integration and miniaturization [6–8].

Mercury, in the form of mercury film electrodes (MFEs) or the hanging mercury drop electrode (HMDE), has been used for trace Tl (I) determination by ASV [9,10]. Due to the toxic effects of mercury and its compounds [11], research efforts have been focused on developing alternative "green" voltammetric sensors. Among these sensors, bismuth [12,13], antimony [14–16], lead [17,18] and selenium film electrodes [19] have proved quite successful for trace metals voltammetric detection. Regarding Tl(I) determination, different ASV analytical protocols have been developed for antimony film electrodes (SbFEs) [16,20] and bismuth film electrodes (BiFEs) [21,22]. The tin film electrode (SnFE) is the latest addition in the family of non-toxic transducers, although its electroanalytical properties are at an initial stage of investigation with good prospects [23–29]. However, only one report of SnFE has appeared in the literature dealing with the determination of Tl(I) by ASV [25]. The approach commonly followed for the formation of metal film electrodes involves in situ or ex situ electrochemical plating by reduction of respective metal cations to their metallic state on a suitable supporting material [14–28]. Nevertheless, the use of electroplating protocols causes major difficulties associated with the generation and maintenance of the metallic layer, that serves as the active electrode surface. More specifically, the surface of the metallic layer and consequently the analytical performance of the electrode are critically dependent on the nature of supporting electrolyte, the pH of the solution, the concentration of the respective metal cations and the nature of the conductive supporting substrate [25,29].

In this work, we report the fabrication of an electroanalytical device with on-chip metal film electrodes. This microsensor features a Sn working electrode, a Ag reference electrode and a Pt counter electrode, all formed by sputtering films of the respective metals on an oxidized silicon chip. The use of microengineering technologies

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for the fabrication of the proposed microsensors overcomes the main problems of electroplating approach, ensures strict control and reproducibility of the surface morphology and offers the potential for mass-production of inexpensive and disposable sensors. In addition, the incorporation of all three electrodes in an integrated device is ideal for field analysis that requires miniaturized transducers. The proposed tin sensors were successfully applied to the determination of Tl(I) by SWASV and were shown to exhibit enhanced performance in media of low pH.

2. Experimental

2.1. Reagents

All the chemicals were of analytical grade. Doubly distilled water was used throughout. Working metal ion solutions were prepared from 1000 mg L^{-1} atomic absorption standard solutions after appropriate dilution with water. The working solutions were made in 0.05 mol L^{-1} nitric acid supporting electrolyte. A 5×10^{-3} mol L^{-1} stock solution of the disodium salt of EDTA, a 1 mol L^{-1} stock solution of KCl and a 1000 mg L^{-1} stock solution of Triton X-100 (BDH, Poole, England) were prepared in water. The metal targets were of 99.9% purity (Williams Advanced Materials, Buffalo, NY).

2.2. Instrumentation

All electrochemical experiments were carried out with an electrochemical analyzer PGSTAT101 (Metrohm Autolab, Utrecht, The Netherlands) connected to a personal computer. A magnetic stirrer operating at approximately 1000 rpm provided stirring during the deposition step. Baseline correction of the resulting voltammograms was performed using the NOVA 1.8 software (Metrohm Autolab). The morphology of the metal deposits was observed with an atomic force microscope (AFM) (SPM SMENA, NT-MDT Co., Moscow, Russia). An optical microscope (Karl Suss PA 200, SUSS MicroTec, Garching, Germany) was used for imaging the surface of the tin working electrode. A thin film deposition system (CV401, Cooke Vacuum Products, South Norwalk, CT) was used for the sputter deposition process.

2.3. Fabrication of sensors

A schematic diagram of the sensor is illustrated in Fig. 1. An aluminum mask featuring slots for the three electrodes was attached firmly to an oxidized (900 nm SiO_2) silicon wafer (5" in diameter, 500 μm in thickness, Si-Mat silicon materials, Kaufering, Germany). Titanium was first sputtered on the counter and the reference electrode at respective slots to a thickness of 5 nm and then, three electrodes were formed by sputtering each metal (400 nm Ag, 400 nm Pt and 400 nm Sn) on the wafer at the respective slots, by covering the other two slots with a plastic sheet. As soon as the three electrodes were formed, the sensing area of the device was isolated from the contact/grip pads by a simple photolithographic step, using AZ5214 photoresist (EZ-EM Materials). The final dimensions of the planar electrodes were (length × width, in mm):WE 5 × 5; CE 3 × 5; RE 3 × 5. Connection of the sensor to the potentiostat was accomplished by crocodile clips. Bismuth and antimony microsensors used for comparative studies were fabricated according to our previous works [30,31].

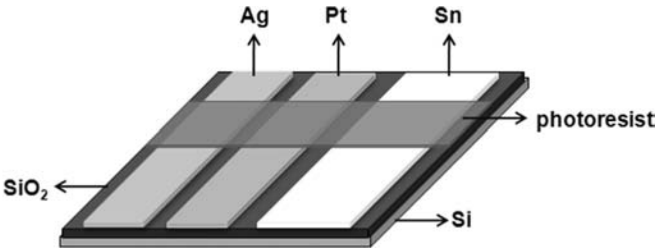

Fig. 1. Schematic diagram of tin mini-device.

2.4. Measurement procedure

The sample was spiked with KCl to a final concentration of 1×10^{-3} mol L^{-1} in order to stabilize the potential of the on-chip reference electrode. The sensor was immersed into the sample solution and the preconcentration was carried out at −1.30 V for a predefined time period in stirred solution. After the accumulation, a SW voltammetric scan (initial potential, −0.90 V; final potential, −0.57 V; frequency, 50 Hz; pulse height, 40 mV; step, 4 mV) was applied to the working electrode and the voltammogram was recorded. Then, the electrode was cleaned for traces of remaining accumulated metal for 10 s at −0.57 V. This potential was sufficiently anodic to oxidize traces of Tl remaining on the electrode surface after the anodic scan, and sufficiently cathodic to prevent oxidation of tin film. Quantification was performed by standard additions of Tl(I).

3. Results and discussion

3.1. Electrochemical and optical characterization of the tin working electrode

Acidic media ($pH \leq 2$) are usually required in order to prevent analyte loss due to the hydrolysis processes that may occur during the storage and treatment of samples and to release metals from complexes with naturally-occurring organic acids. Therefore, sensor operation in acidic media is considered useful for direct sample analysis. The SbFE is credited with enhanced performance at low pHs compared to the BiFE [15,20,32]. In order to demonstrate the suitability of the proposed tin microsensors for ASV measurements in relatively strong acidic media, the detection of Tl(I) by SWASV was studied in 0.05 mol L^{-1} nitric acid solution. It is underlined that the existing applications of SnFEs (the majority of them prepared via the in situ electroplating protocol on various forms of carbon [23–27] or gold [28] substrates) to the voltammetric determination of trace metals utilize moderately acidic conditions (acetate buffer (pH 3.9–5.3)) and only one report deals with the determination of Tl(I) [25].

The potential window of the microfabricated tin sensor was studied in the DC voltammetric mode by scanning the potential in the range −1.40 to −0.40 V in 0.05 mol L^{-1} HNO_3 and 0.1 mol L^{-1} acetate buffer (pH 4.5) (Fig. 2). Oxidation of tin started to occur at the anodic side of voltammograms with the onset of the oxidation process depending on the pH: −0.50 V for the nitric acid and −0.62 V for the acetate buffer, while the cathodic limit was set by the reduction of hydroxonium ions. The sensors exhibited well-defined stripping signals for Tl(I) with low background current contributions in both supporting electrolytes, presenting similar sensitivity (Fig. 2-inset). It is noted that tin electrodes present a narrower anodic useful potential window compared to Hg, Bi and Sb electrodes, as Sn is oxidized at more negative potentials [29]; however, the use of highly acidic media extends the anodic potential range of the tin electrode.

Microscopic inspection with optical microscopy at different areas of the sensor indicated the completed coverage of the surface, with no bare SiO_2 areas visible. Ag and Pt layers, when examined with AFM, exhibited similar morphology of their surfaces with average roughness of about 10 nm (Fig. 3(A)). In contrast, the tin surface was rougher with an average roughness

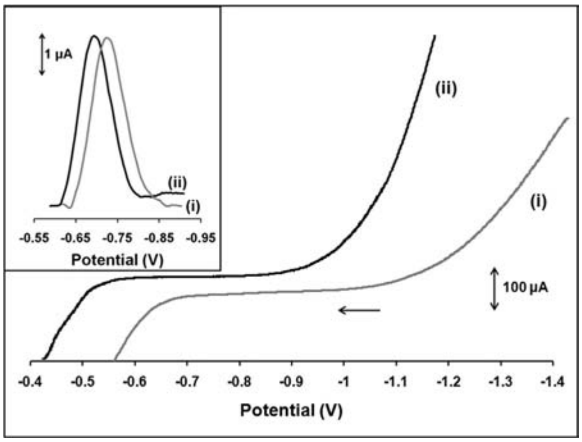

Fig. 2. DC voltammograms taken on the Sn sensor in: (i) 0.1 mol L^{-1} acetate buffer (pH 4.5); (ii) 0.05 mol L^{-1} HNO_3. Scan rate 50 mV s^{-1}. (Inset) Comparative SWASV voltammograms of solutions containing 10 μg L^{-1} of Tl(I) at the Sn sensor in: (i) 0.1 mol L^{-1} acetate buffer (pH 4.5); (ii) 0.05 mol L^{-1} HNO_3. Other conditions: deposition potential: −1.30 V; deposition time: 240 s; frequency: 50 Hz; pulse height: 40 mV; and step increment: 4 mV.

of 130 nm, leading to an increase in the active surface area of the sensor (Fig. 3(B)). The tin surface morphology is similar to that of sputtered bismuth and differs from that of sputtered antimony, as the roughness of the sputtered film surface depends on the melting point of each metal [31].

The microfabricated Sn sensor was compared to a sputtered BiFE and a SbFE, in terms of their respective stripping response for Tl(I) using SWASV. Comparative stripping voltammograms of a solution containing 10 μg L^{-1} of Tl(I) in 0.05 mol L^{-1} HNO_3 on the three sensors are illustrated in Fig. 4. On the Sn sensor, the Tl peak potential was shifted to more positive potentials, while the Tl stripping peak was sharper and narrower compared to the sputtered BiFE and SbFE, proving the good performance of tin sensors in strongly acid media.

3.2. *Effect of the preconcentration potential, preconcentration time and square-wave parameters*

The effect of the deposition potential in the range −0.70 V to −1.30 V on the stripping current of Tl(I) was studied in a solution containing 20 μg L^{-1} of Tl(I) in 0.05 mol L^{-1} nitric acid and the results obtained are presented in Fig. 5(A). The expected sigmoidal shape was observed for Tl stripping currents: the stripping responses were negligible at potentials more positive than −0.70 V and increased rapidly as the deposition potential became more negative until −1.30 V. Deposition potential of −1.30 V was selected as the optimum, since more positive potentials were inefficient for reduction of thallium, while more negative potentials can cause hydrogen evolution (in view of the low pH medium used) which interferes with the deposition of Tl onto the electrode surface.

The electrolytic preconcentration time was studied in the range 60–600 s for a solution containing 20 μg L^{-1} Tl(I) in 0.05 mol L^{-1} nitric acid. The stripping currents followed a typical rectilinear dependence on the deposition time with a rapid increase in the response at low deposition times and gradual levelling-off as saturation of the electrode was eventually reached, as shown in Fig. 5(B). A preconcentration time of 240 s was selected in order to achieve a satisfactory compromise between high sensitivity and short analysis times.

SW parameters including SW frequency, SW step increment and SW pulse height were investigated in a solution containing

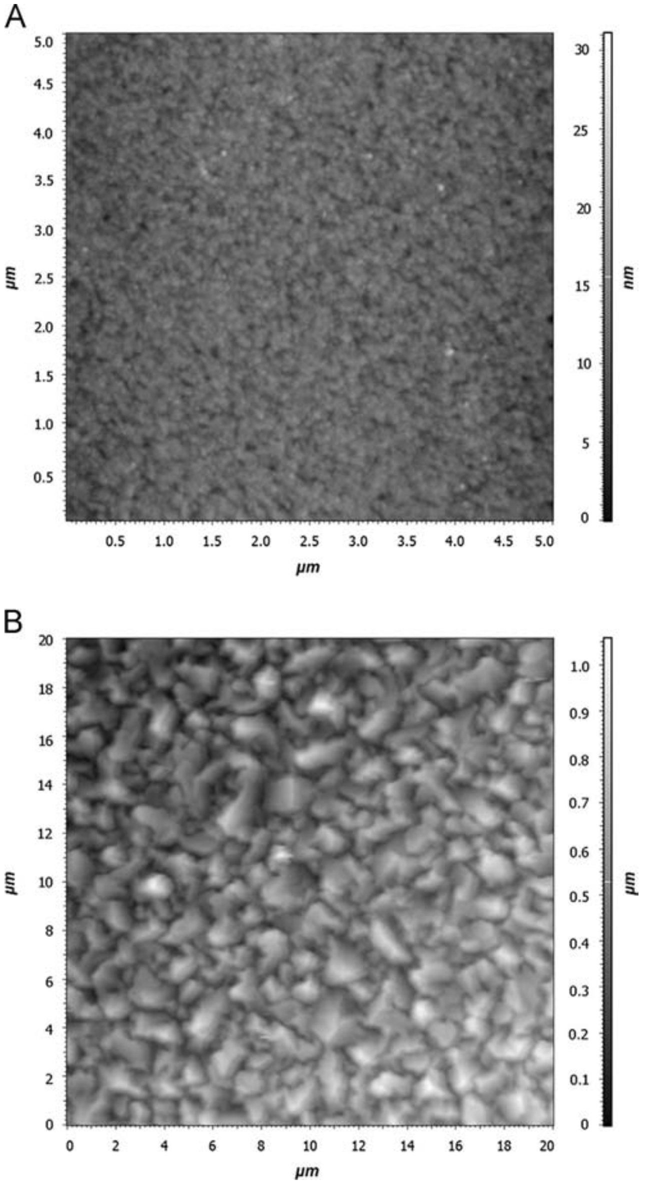

Fig. 3. (A) AFM image of the Pt counter electrode. (B) AFM image of the Sn working electrode.

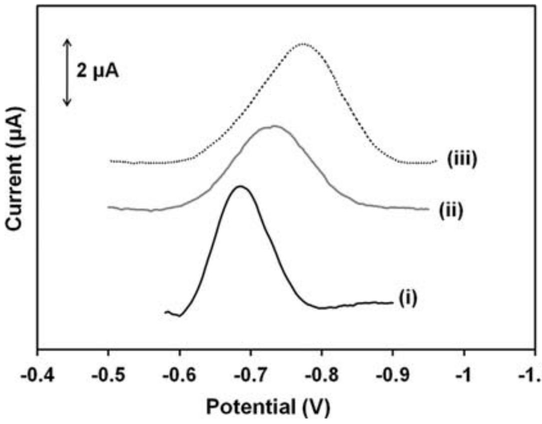

Fig. 4. Comparative SW voltammograms of a solution containing 10 μg L^{-1} Tl(I) in 0.05 mol L^{-1} HNO_3 on microfabricated sensors: (i) Sn; (ii) Bi; and (iii) Sb. Other conditions as in Fig. 2.

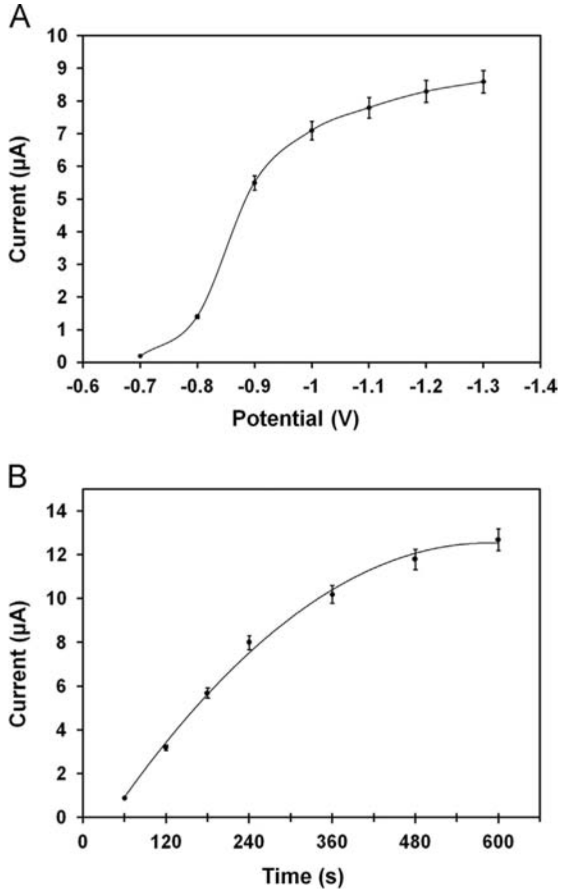

Fig. 5. (A) Effect of the deposition potential on the peak height of Tl for a solution containing 20 μg L^{-1} of Tl(I) at the microfabricated Sn sensor. (B) Effect of the deposition time on the peak height of Tl for a solution containing 20 μg L^{-1} of Tl(I) at the microfabricated Sn sensor. Each point represents the mean value ± sd (n=3). Other conditions as in Fig. 2.

20 μg L^{-1} of Tl(I) in 0.05 mol L^{-1} nitric acid. The effect of the frequency was studied in the range 12.5–100 Hz. As the frequency increased, the Tl stripping peak current increased up to 50 Hz and remained stable up to 100 Hz, while at higher frequencies the background increased due to the contribution of capacitive current. The effect of the SW pulse height was studied in the range from 10 to 80 mV. The Tl peak height increased with increasing pulse height but the background deteriorated and the peak width increased for pulse height higher than 40 mV. The SW step increment was investigated in the range 1–16 mV. The Tl stripping peak height was unaffected by the variation in the step increment, while the background increased considerably at higher values of the scan increment. The best compromise among sensitivity, peak sharpness and background characteristics was obtained at a frequency of 50 Hz, step increment of 4 mV and pulse height of 40 mV. Thus, these square wave parameters were finally selected for further work.

3.3. Calibration features – stability of sensor

The analytical utility of the proposed tin mini-device was assessed for the determination of Tl(I) by SWASV, under the following conditions: supporting electrolyte, 0.05 mol L^{-1} HNO_3; deposition potential, −1.30 V; deposition time, 240 s; frequency, 50 Hz; pulse height, 40 mV; and step increment, 4 mV. Voltammograms for the determination of Tl(I) in the concentration range 0–80 μg L^{-1} are illustrated in Fig. 6(A). The calibration curve was expressed by the following first-order equation:

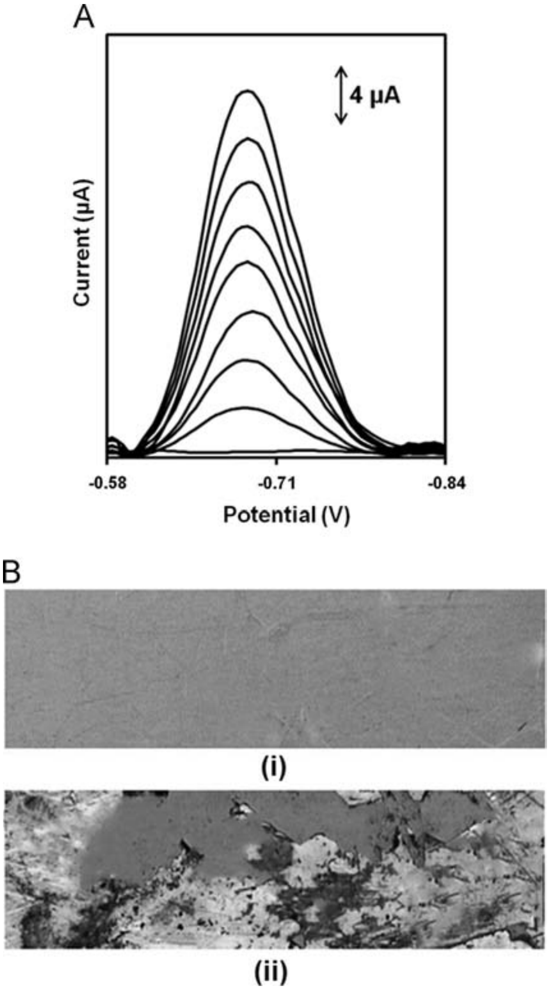

Fig. 6. (A) A series of SW voltammograms taken at the Sn sensor for increasing concentrations of Tl(I). From below: blank and 8 successive additions of 10 μg L^{-1} of Tl(I). Other conditions as in Fig. 2. (B) Optical micrographs of the Sn sensor: (i) before use; (ii) after 16 preconcentration/stripping cycles.

$$I_{\mathrm{Tl}}(\mu\mathrm{A}) = (0.37 \pm 0.005)[\mathrm{Tl(I)}](\mu\mathrm{g\ L}^{-1}) + (0.69 \pm 0.28), \quad r^2 = 0.998$$

The limit of detection, calculated as the concentration of Tl(I) corresponding to three times the standard deviation of the signal of the lowest concentration level, was 1.1 μg L^{-1}. The limit of detection is comparable with that at the in situ plated SbFE [16,20] in acidic solutions. The within-sensor reproducibility (expressed as the % relative standard deviation at the same sensor (n=10)) was 5.2% at the 10 μg L^{-1} level. The between-sensor reproducibility (expressed as the % relative standard deviation at eight different sensors) was 12.8% at the 10 μg L^{-1} level. These results demonstrate the suitability of the tin microsensor for measuring selected trace heavy metal ions in acidic media and in the presence of dissolved oxygen.

The shelf-life of the devices was examined within a period of at least 10 months following their fabrication. The devices did not exhibit any changes in the appearance, color and surface morphology, while the electroanalytical response remained stable. Microscopic examination of the Sn working electrode, after prolonged use in 0.05 mol L^{-1} HNO_3 showed erosion of its surface which led to inactivation of the sensor and gradual decrease of its response (Fig. 6(B)). Each sensor could be used for at least 12 preconcentration/stripping cycles in the semi-disposable mode.

3.4. Interference study

In this work, the effect of different concentrations of heavy metals known to interfere with the determination of Tl(I) (i.e. Cu(II), In(III), Cd(II)) was investigated on the stripping response of Tl(I) in 0.05 mol L^{-1} HNO$_3$. In(III) and Cd(II) are generally considered as the major interferences in the determination of Tl(I) either on bismuth [33] or antimony electrodes [16], since these metals can readily preconcentrate on these electrodes and produce stripping peaks that overlap with those of Tl. Fig. 7 (A) illustrates stripping voltammograms for 10 μg L^{-1} Tl(I) (Fig. 7A-i), for 10 μg L^{-1} In(III) (Fig. 7A-ii), for 5 μg L^{-1} Cd(II) (Fig. 7A-iii) and for 10 μg L^{-1} Tl(I) in the presence of 10 μg L^{-1} In (III) and 5 μg L^{-1} Cd(II) (Fig. 7A-iv). The three peaks were not sufficiently resolved to allow determination of Tl(I) and therefore the simultaneous determination of Tl(I) and Cd(II), or Tl(I) and In (III) is not possible on the tin sensor. However, the interference caused by multi-valent cations was alleviated effectively by the addition of EDTA that forms stable complexes only with multi-valent cations [33,34]. With the addition of 5 × 10^{-6} mol L^{-1} of EDTA the peaks of Cd and In practically disappeared, while the peak of Tl remained unaffected (Fig. 7A-v). Moreover, the interference of Cu(II) on the Tl stripping peak was evident at the tin sensor even at a Cu(II)-to-Tl(I) concentration ratio of 3:1 and was more severe as the ratio of Cu(II)-to-Tl(I) concentration increased, but the presence of EDTA also alleviated the interference by Cu(II). Fig. 7(B) shows a series of stripping voltammograms in the range 10–50 μg L^{-1} Tl(I) in the presence of 50 μg L^{-1} Cd(II), Cu(II) and In (III) after addition of 2 × 10^{-5} mol L^{-1} of EDTA. The addition of EDTA was sufficient to alleviate the interference caused of Cd(II), Cu(II) and In(III), without affecting the sensitivity and the linearity of the respective calibration curve. The presence of other common cations such as Ba(II), Ca(II), Mg(II), Co(II), Ni(II), Na(I), and K(I), at a ten-fold excess over Tl(I) did not affect the stripping peaks of Tl.

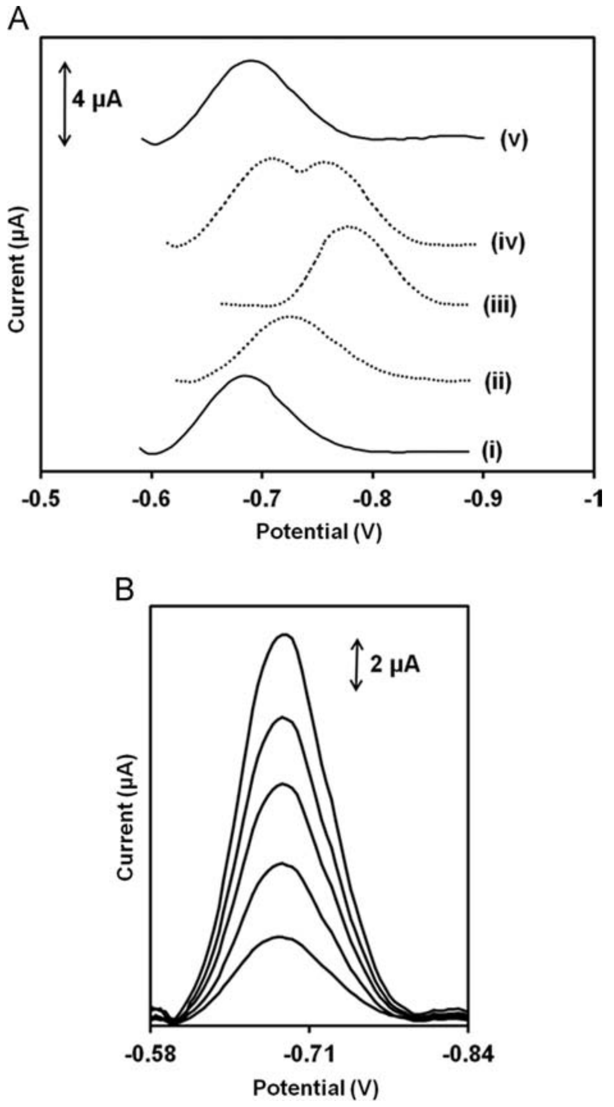

Fig. 7. (A) Comparative SW voltammograms obtained at the microfabricated Sn sensor in a solution containing: (i) 10 μg L^{-1} of Tl(I); (ii) 10 μg L^{-1} of In(III); (iii) 5 μg L^{-1} of Cd(II); (iv) 10 μg L^{-1} of Tl(I) + 10 μg L^{-1} of In(III) + 5 μg L^{-1} of Cd(II); and (v) as (iv) with 5 × 10^{-6} mol L^{-1} of EDTA. (B) A series of SW voltammograms obtained at the Sn sensor for increasing concentrations of Tl(I) (in steps of 10 μg L^{-1}) in the presence of 50 μg L^{-1} of In(III), Cd(II) and Cu(II) after addition of 2 × 10^{-5} mol L^{-1} of EDTA. Other conditions as in Fig. 2.

The presence of surface-active compounds is another serious interference in stripping analysis since such compounds can easily adsorb on the electrode and inactive its surface [33]. Triton X-100 (a non-ionic surfactant) was selected as a “model” compound to study the effect of the surfactant on the stripping response of Tl on micro-SnFEs. It was found the Tl stripping peak height was suppressed by 22%, 73% and 84% in the presence of 0.1, 0.5 and 1 mg L^{-1} of Triton X-100, respectively.

3.5. Application

The proposed microsensors were assessed by applying them for the determination of Tl(I) in an acidic certified lake water sample (TM 24.3, Environment Canada, Burlington, Canada). The certified lake water sample was preserved with 0.2% w/v nitric acid (~0.03 mol L^{-1}) and the sample contained Cd(II), Cu(II) and Pb(II) with certified concentrations of 2.5, 9.1 and 3.2 μg L^{-1}, respectively. 10 mL of lake water sample was spiked with EDTA to a final concentration of 2 × 10^{-5} mol L^{-1} (in order to complex the multi-valent cations) and with KCl to a final concentration of 1 × 10^{-3} mol L^{-1} and the solution was subjected to analysis with no further treatment. Representative SW voltammograms for the determination of Tl(I) in the lake water sample are illustrated in Fig. 8 and the standard additions plot is shown as an inset. The Tl(I) concentration determined was 3.9 ± 0.3 μg L^{-1} (n=3) which compared well to the reference value of 3.8 μg L^{-1}.

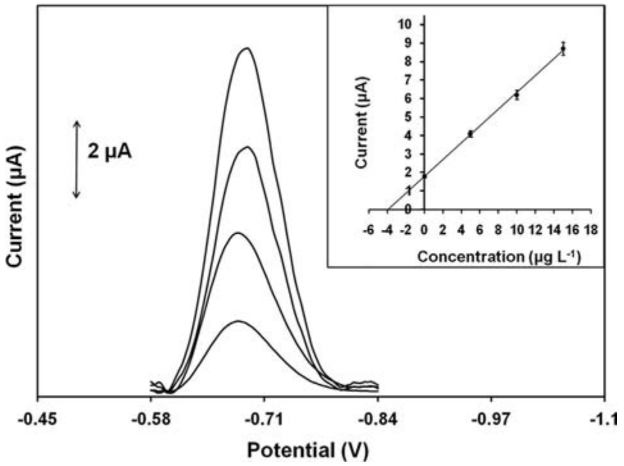

Fig. 8. SW voltammograms for the determination of Tl(I) in a certified lake water sample on tin mini-device. From below: sample and 3 standard additions of 5 μg L^{-1} Tl (I). (Inset) Standard additions curve. Each point represents the mean value ± sd (n=3). Other conditions as in Fig. 2 with addition of 2 × 10^{-5} mol L^{-1} EDTA.

4. Conclusion

In this article, the fabrication of a new type of a tin film mini-device featuring on-chip electrodes is presented and its analytical utility is demonstrated for the determination of Tl(I) in acidic media by ASV. The interference caused by Cd(II) and In(III) was alleviated by the addition of EDTA, since the tin sensor is not suitable for the simultaneous determination of these species in a single assay. These sensors are environment friendly, disposable, easily mass-produced and are ideally suited for field measurements.

Acknowledgments

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