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Development of a "Green" Paper-Based Voltammetric Platform for On-Site Assay of Tl(I) †

Katerina Kouseri [1], Irini Panagiotopoulou [1], Dionysios Soulis [1], Anastasios Economou [1,*], Mamas Prodromidis [2] and Christos Kokkinos [1]

[1] Department of Chemistry, National and Kapodistrian University of Athens, Athens 157 71, Greece; k.kouseri9@gmail.com (K.K.), irinipanagiotopoulou00@yahoo.com (I.P.), dsoulis1@gmail.com (D.S.), aeconomo@chem.uoa.gr (A.E.), christok@chem.uoa.gr (C.K.)

[2] Department of Chemistry, University of Ioannina, Ioannina 45 110, Greece; mprodrom@uoi.gr

* Correspondence: aeconomo@chem.uoa.gr; Tel.: +30 210 7274298

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Abstract: In this work, a "green" electrochemical paper-based device (ePAD) for the voltammetric determination of Tl(I) is described. A mini voltammetric cell was patterned on chromatographic paper using screen-printing to deposit three carbon electrodes and plotting with a hydrophobic ink to from a circular assay zone. The sample was added to the assay zone (which was pre-loaded with Bi(III)) and Tl(I) is quantified by anodic stripping voltammetry (ASV). The experimental conditions and the potential interferences were studied. The limit of detection was at the low μg L^{-1} level, indicating that these devices can serve successfully as fit-for-purpose disposable voltammetric sensors for Tl(I).

Keywords: paper-based; anodic stripping voltammetry; thallium; pen-plotting; screen-printing

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1. Introduction

Thallium is a very toxic metal which interferes with vital processes in living organisms and can cause acute and chronic poisoning [1]. Thallium is present in environmental samples at low concentrations, therefore sensitive analytical methods are required for its determination [2].

Different atomic spectroscopy and chromatography methods are usually employed for thallium quantification in environmental and biological samples but these techniques require expensive and bulky equipment and trained personnel [2]. In contrast, electrochemical techniques require low-cost portable instrumentation with low power requirements, therefore they are better suited to on-site assays; in particular, anodic stripping voltammetry (ASV) is widely used for trace heavy metals determination due to its high sensitivity [3]. Traditionally, mercury electrodes have been used for the determination of Tl(I) by ASV, but, over the last years, alternative "green" electrode materials, including bismuth [4], antimony [5] and tin [6], have been developed and successfully applied to the ASV determination of Tl(I).

On the other hand, paper-based analytical devices (PADs) have gained increased attention in the last fifteen years as low-cost, portable sensing modules for a variety of analytical applications, capitalizing on the advantages of cellulose paper as a functional platform [7,8]. In particular, electrochemical PADs (ePADs) are attractive analytical devices that combine the advantages of cellulose as a platform and electrochemistry as a detection approach [9]. Only a limited number of PADs have been developed for the determination of selected trace metals by ASV [10] but the determination of Tl(I) has not been reported so far.

This work describes a new type of paper-based electrochemical platform for the rapid trace determination of Tl(I). The sensing platform is based on the patterning of a mini voltammetric cell on chromatographic paper consisting of: (a) three carbon electrodes deposited on paper by screen-printing, and (b) a circular assay zone formed by plotting with a hydrophobic marker pain. The combination of screen-printing [11] with pen-plotting [12] in paper devices enables the low-cost and fast large-scale fabrication of ePADS. Tl(I) was quantified by ASV on the ePAD which was previously modified with Bi(III).

2. Experimental

2.1. Reagents and Materials

All chemicals used for the preparation of stock and standard solutions were of analytical reagent grade and purchased from Sigma-Aldrich. Doubly-distilled water was used throughout.

The paper support was chromatography paper Macherey-Nagel MN 261. A hydrophobic marker pen (Edding 780 0.8 mm tip thickness (black)) was used for plotting the circular PADs. A graphite ink (Loctite EDAG 423SS, Henkel, Belgium) was used for patterning of the electrodes by screen-printing.

2.2. Instrumentation

A Palmsens potentiostat controlled by the PSTrace 5.5 software (Palmsens, Houten, Netherlands) was used for the electrochemical experiments.

For the fabrication of the screen-printed electrodes, a semi-automatic screen printer (E2, EKRA) was used.

The circular PADs were drawn using the open-access software Inkscape (Inkscape Project, https://inkscape.org/about/). The AxiDraw extension for Inkscape was used for controlling an AxiDraw desktop x-y plotter (Evil Mad Science LLC, Sunnyvale, CA) connected to a PC via a USB interface.

2.3. ePAD fabrication

The fabrication of the ePADs is illustrated in Figure 1. Arrays of graphite ink three-electrode electrochemical cells were deposited on paper by screen-printing. Then, the PADs were drawn on the paper substrate using pen-plotting and left at room temperature for 10 min before use. The pattern was repeated on the reverse side of the paper after aligning the paper.

2.4. Experimental procedure

For the detection of Tl(I), the assay zone is pre-loaded with a Bi(III) solution and dried. 50 μL of the 20 mg L^{-1} Bi(III) standard solution was applied to circular ePAD and allowed to dry at room temperature.

Then, 40 μL of the sample was spiked with 10 μL of a 5 mol L^{-1} acetate buffer (pH 4.5) and the solution was placed at the circular ePAD. The electrodes were connected to the potentiostat and accumulation was carried out at -2.5 V for 420 s *vs* the carbon pseudo-reference electrode. The Tl(I) in the sample and the pre-loaded Bi(III) accumulated *in situ* on the working electrode forming an alloy according to the reaction:

$$\mathrm{Tl(I) + Bi(III) + 4e^- \rightarrow Tl(Bi)}$$

Finally, an anodic scan from -1.5 V to -0.2 V was applied in the differential-pulse (DP) mode (scan rate, 10 mV s^{-1}; step, 5 mV; pulse height, 25 mV) during which the accumulated thallium and bismuth oxidized according to the reactions:

$$\mathrm{Tl(Bi) \rightarrow Tl(I) + e^-}$$

$$\mathrm{Bi \rightarrow Bi(III) + 3e^-}$$

giving rise to separate stripping peaks and the voltammogram was recorded.

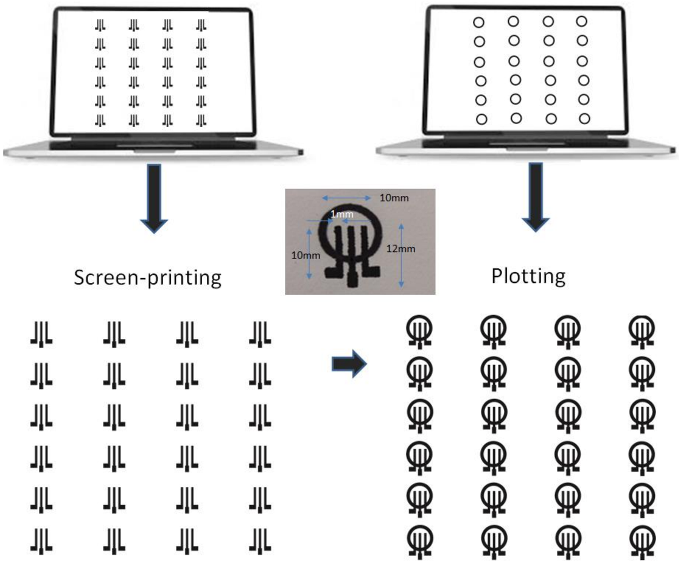

Figure 1. The fabrication process of the ePADs (a single ePAD with dimensions is shown as an insert). The center electrode is the working electrode (WE) while the other two electrodes serve as the reference electrode (RE) and the counter electrode (CE).

3. Results and discussion

The method optimization involved study of the supporting electrolyte, the Bi(III) concentration, the deposition time and the deposition potential. Five supporting electrolytes (0.5 mol L^{-1} of HCl, HNO_3 and H_2SO_4 was well as 0.1 and 1.0 mol L^{-1} of acetate buffer (pH 4.5)) were studied. The best defined and highest peak for both Tl was obtained in 1.0 mol L^{-1} of acetate buffer (pH 4.5) which was selected as the supporting electrolyte. The variation of the Tl stripping peak heigh with the deposition time was studied between 60 and 420 s; the Tl signal increased in the range 0-240- s and then reached a plateau so that 240 s was selected. The effect of the deposition potential on the Tl striping peak height was studied in the range -1.0 to -3.0 V. The Tl signal increased almost linearly between -1.0 v and -2.5 V and then levelled off, therefore -2.5 V was selected as the deposition potential. The effect of the Bi(III) solution concentration pre-loaded on the ePAD for the *in-situ* formation of the bimuth film on the Tl signal was finally investigated. The Tl stripping signal increased as the concentration of Bi(III) increased in the range 1-20 mg L^{-1} and remained constant for higher Bi(III) concentrations; thus, 20 mg L^{-1} of Bi(III) was selected for further work.

The effect of heavy metals known to interfere with the determination of Tl(I) (i.e Cu(II), Pb(II) and Cd(II)) was investigated. Cd(II) and Pb(II) gave rise to stripping peaks that overlapped with that of Tl while Cu(II) severely suppressed the Tl stripping peak. The interference caused by multivalent cations was effectively addressed by the addition of EDTA ($\sim 5\times10^{-5}$ mol L^{-1}) which complexes strongly with multivalent ions but not with the monovalent Tl(I) [4].

Calibration for Tl(I) was carried out by DPASV in the concentration range 0-150 μg L^{-1}. Representative voltammograms are illustrated in Figure 2a and the calibration plot (peak current *vs* Tl(I) concentration) is shown in Figure 2b. The limit of detection (LOD) was calculated as 6.1 μg L^{-1} (using the formula $LOD=3.3\times s_b/S$ (where s_b is the standard deviation of the intercept of the calibration plot and S is the slope of the calibration plot). The assay reproducibility was calculated by performing measurements with a solution containing 100 μg L^{-1} of Tl(I) at 6 PADs; the % relative standard deviations was 15.1 %. These figures of merit are considered adequate for disposable sensors intended for rapid low-cost sensing purposes.

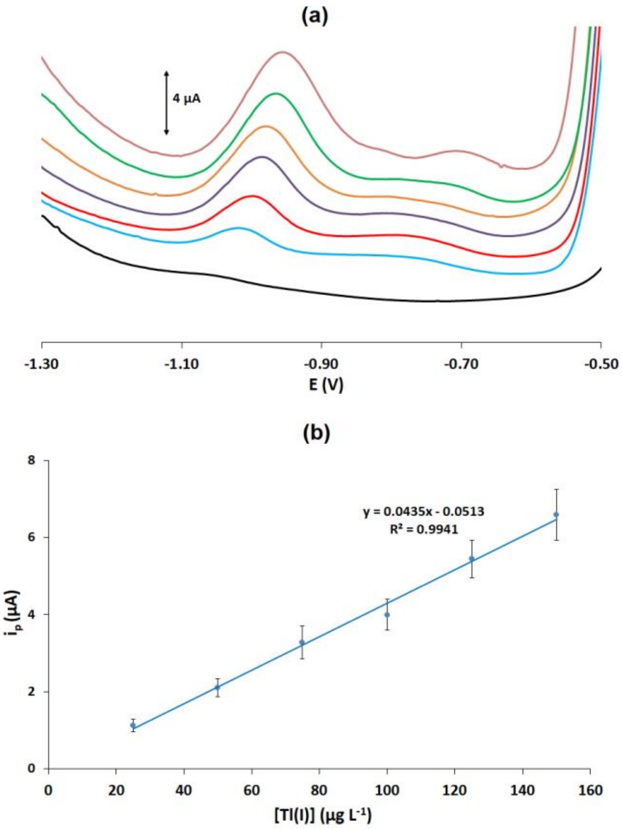

Figure 2. (a) DPASV traces of Tl(I) in the concentration range 0-150 μg L^{-1} (the bottom trace corresponds to the blank), (b) calibration curve for Tl(I).

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