



Paper-based device with a sputtered tin-film electrode for the voltammetric determination of Cd(II) and Zn(II)



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ABSTRACT

This work describes a microfabricated electrochemical paper-based analytical device (ePAD) for the simultaneous voltammetric determination of Cd(II) and Zn(II) at trace levels. The ePAD integrates a wax-printed microfluidic channel and, on the reverse side of the paper, sputtered thin films of Sn, Pt and Ag serving as the working, counter and reference electrodes, respectively. The microfluidic channel ensures electrolytic contact between the electrodes with only 10 μL of working solution. The determination of Cd(II) and Zn(II) is performed at the 400 nm-thick sputtered Sn-film working electrode, in a pump-free and unstirred mode, by anodic stripping voltammetry. Under the selected conditions, the limits of detection were 0.9 $\mu\text{g L}^{-1}$ Cd(II) and 1.1 $\mu\text{g L}^{-1}$ Zn(II) and the between-sensor reproducibility was 5.7% for Cd(II) and 7.5% for Zn(II) at the 30 $\mu\text{g L}^{-1}$ level ($n = 5$). The ePAD costs only 0.11\$ and presents favorable fabrication and operational features, that make it suitable for simple, fast and on-site analysis.

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1. Introduction

Heavy metals are significant pollutants existing at trace levels in environmental samples and, therefore, sensitive methods are required for their determination [1]. Compared to spectroscopic methods which are expensive, complicated and cannot be applied in field measurements, electrochemical approaches offer fast, ultrasensitive, and on-site determination of heavy metals, with negligible power consumption. In particular, anodic stripping voltammetry (ASV) is the most powerful technique for trace metal analysis, thanks to its excellent sensitivity stemming from a preconcentration step in conjunction with different appropriate electrode materials [2]. For many years, mercury electrodes have been the most widely applied transducers in ASV, but more recently, less toxic bismuth and antimony sensors have been introduced [3–5]. In 2007, tin-film electrodes have been added in this group of mercury-free transducers, offering attractive electroanalytical characteristics especially for Cd(II) and Zn(II) determination [6–13]. Commonly, the majority of electrodes modified with metal-films are prepared via electroplating protocols on carbon supports [3–11]. Electroplating requires high concentrations of metal-containing plating solutions and the structure of the electro-

plated metal film exhibits surface structure that strongly depends on the experimental variables (i.e. concentration of the plating solution, pH of the working solution, deposition potential and deposition time) [13,14]. An alternative approach for the fabrication of thin metal-film electrodes, proposed by our group, is by sputtering of a metal film on silicon and polyimide substrates; sputtering enables the parallel fabrication of many devices with highly reproducible geometrical characteristics and strictly controlled surface morphology [13,14].

Over the past decade, the progress in micro- and nano-technology has facilitated the miniaturization of conventional and bench-type instrumentation towards the development of low-cost, and simple lab-on-a-chip sensing platforms that enable rapid on-site analysis [15–17]. The use of paper as a substrate for the fabrication of lab-on-a-chip devices is advantageous because paper is available at low cost, is biodegradable, is readily available in various qualities, can be easily patterned and enables the autonomous (pump-free) fluid transport through capillary action. By exploiting these attributes, several electrochemical paper-based analytical devices (ePADs) have been developed and applied in biosensing through enzymatic labeling [16,17]. Nevertheless, the application field of ePADs to ASV determination of heavy metals can be considered largely unexplored, since only a few reports have appeared in the literature dealing with the determination of Pb(II) and Cd(II) [e.g. 18–20]. Moreover, in these ASV-ePADs, the working electrodes

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are made of carbon or boron doped diamond produced by stencil or screen-printing and in situ electroplated with bismuth.

This work describes an alternative type of ePAD with integrated sputtered film electrodes for the fast, micro-volume and simultaneous ASV determination of Cd(II) and Zn(II) at trace levels. The device integrates a wax-printed channel and, on the reverse side of the paper, a voltammetric cell which is composed of sputtered thin films of a Sn (working electrode, WE), Ag (reference electrode, RE) and Pt (counter electrode, CE). The ePADs were successfully applied to the ASV determination of Cd(II) and Zn(II) at trace levels. This microfluidic paper chip presents significant advantages in terms of cost, fabrication and operational characteristics over conventional electrochemical ASV sensors and existing ePADs offering high sensitivity and requiring minimum sample volumes (typically 10 μL of working solution).

2. Experimental section

2.1. Reagents and apparatus

Xerox Genuine solid ink was used for wax-printing on Whatman No. 1 chromatography paper using a Xerox 8570DN solid ink printer. Metal targets for sputtering were of 99.9% purity (Williams Advanced Materials) and all the other reagents were from Sigma-Aldrich. Stock metal ion solutions were prepared from 1000 mg L^{-1} atomic absorption standard after dilution with doubly-distilled water. The working solutions were made in 0.1 mol L^{-1} acetate buffer (pH 4.5) containing 1 mmol L^{-1} KCl (supporting electrolyte). The Cl(I) ions were used in order to stabilize the potential of reference electrode.

A portable EmStat potentiostat (PalmSens) equipped with the PSTrace 4.2 software was used for the square wave anodic stripping voltammetry (SWASV). Connection of the ePAD to the potentiostat was accomplished by three crocodile clips from PalmSens. The sputtering system was the CV401 (Cooke Vacuum Products) and a field emission scanning electron microscope (FESEM) (JEOL JSM-7401f) was used for the inspection of the Sn film on paper surface.

2.2. Measurement procedure

A portion of 10 μL of working solution containing specific concentrations of Cd(II) and Zn(II) was added in the circular zone of the microfluidic channel of the ePAD (on the reverse side of the paper from which the electrodes were deposited) and Zn(II) and Cd(II) were preconcentrated on the Sn-film WE at -1.50 V for 120 s (Fig. 1). The potential of the WE was then scanned from -1.30 to -0.65 V and the voltammogram was recorded. The SW conditions were: frequency, 50 Hz; pulse height, 40 mV; step increment, 4 mV.

2.3. Fabrication of the ePAD

A photograph of the ePADs and a schematic diagram of the fabrication steps are illustrated in Fig. 1. Initially, the microfluidic channel was printed on the paper substrate by wax-printing. Next, the sputtering process was carried out on the reverse side of paper substrate, using three polyester sheets with a slot of 4 mm in width (Mac Dermid) as pattern masks. The electrodes (Ag, Pt, Sn) were successively sputtered on the paper substrate to a thickness of 400 nm, using each time the specific polyester mask. Finally, the devices were treated in an oven for 1 min at 140°C so that to the wax melted and penetrated the paper, creating the hydrophobic barriers and forming the microfluidic channel.

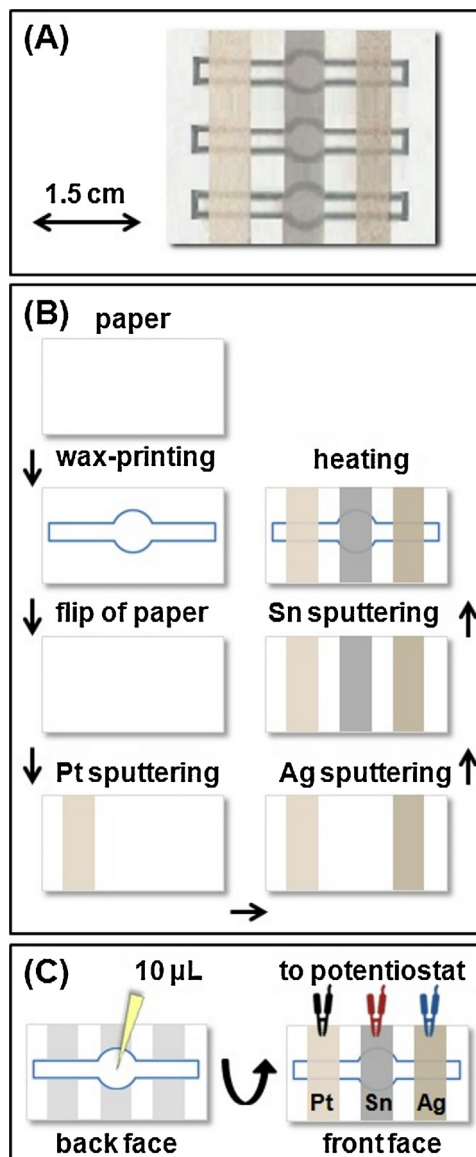


Fig. 1. (A) Photograph of the ePADs. (B) Main steps of the fabrication of the ePAD. (C) Main steps of the measurement procedure.

3. Results and discussion

The selected design of the ePAD enables the reproducible fabrication of low-cost, autonomous and ready-to-use microfluidic devices, which can operate with minimum sample volumes (only 10 μL) and do not require any additional modification before use (i.e. electroplating). At our lab scale 72 devices were simultaneously produced in every fabrication run and the cost of each ePAD was calculated at 0.11\$ (bill of materials per ePAD: 0.009\$ for paper substrate and wax-printing, 0.102\$ for sputtering of the three metals). The microfluidic channel was produced by wax-printing since this is a very simple and cheap patterning technique readily coupled to sputtering enabling the parallel production of a large number of paper devices. The microfluidic channel intended to ensure the electrical communication among the three metal-film electrodes with the minimum volume of electrolyte. The surface characterization of the Sn film WE was performed through FESEM. As shown in the FESEM micrograph in Fig. 2A, the respective whole area of paper substrate was covered with the sputtered Sn film. The Sn film presented a rough surface which is characteristic for metals

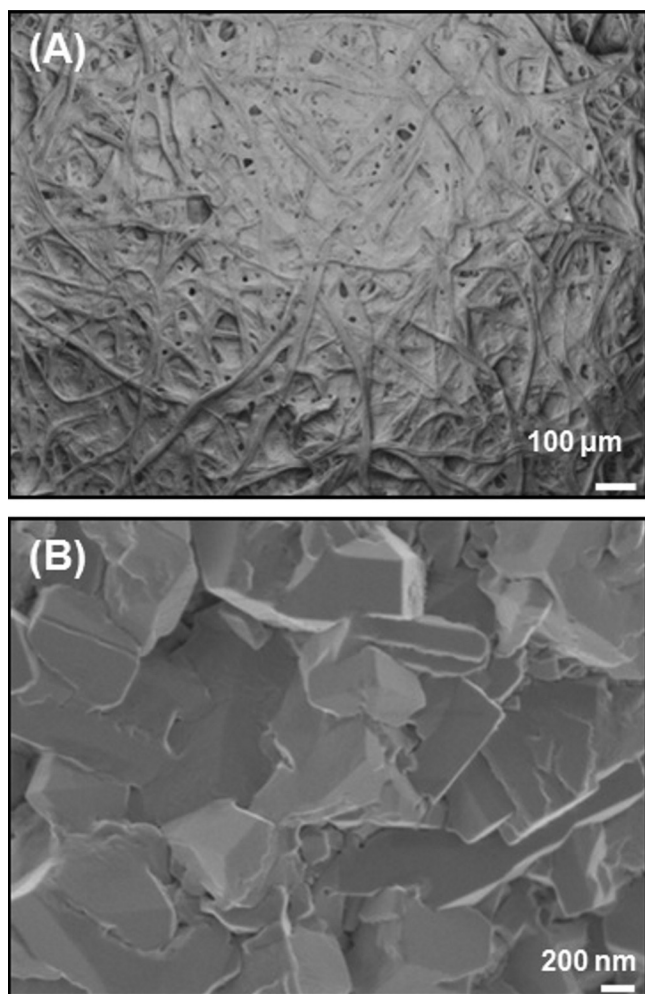


Fig. 2. (A), (B) FESEM images of the Sn WE of the ePAD at two different scales.

with low melting points deposited by sputtering [13], leading to an increase in the active surface area of the sensor (Fig. 2B).

The electroanalytical performance of the ePADs was assessed for the simultaneous determination of Cd(II) and Zn(II) by SWASV. Initially, the effect of the preconcentration potential (in the range of -1.60 V to -0.90 V), preconcentration time (in the range of 30 s to 240 s) and the SW parameters (SW frequency (in the range 12.5–100 Hz), SW step increment (in the range 1–16 mV), SW pulse height (in the range 10–80 mV)) on the SWASV response of Cd(II) and Zn(II) was studied using a solution containing $30 \mu\text{g L}^{-1}$ each of Cd(II) and Zn(II). The best compromise among sensitivity, time of analysis, peak sharpness and background characteristics was obtained at a frequency of 50 Hz, step increment of 4 mV, pulse height of 40 mV, preconcentration time of 120 s and preconcentration potential of -1.50 V. The ePADs exhibited linear calibration plots in the studied concentration range (5 – $40 \mu\text{g L}^{-1}$) for both metal ions with good linearity ($R^2 > 0.99$ for both cations) (Fig. 3). Each ePAD was used for one measurement and five replicate measurements at each concentration level were carried out using five different ePADs. The limits of detection (LODs) (calculated as three times the standard deviation of intercept divided by the slope of calibration plot) were $0.9 \mu\text{g L}^{-1}$ of Cd(II) and $1.1 \mu\text{g L}^{-1}$ of Zn(II). The LODs for Cd(II) and Zn(II) are comparable with those obtained using Sn-film working electrodes operating in conventional large volume electrochemical cells (ranging from $0.5 \mu\text{g L}^{-1}$ to $1.13 \mu\text{g L}^{-1}$ for Cd(II) and from $0.3 \mu\text{g L}^{-1}$ to $5 \mu\text{g L}^{-1}$ for Zn(II)) [6–13]. The LOD of Cd(II) is comparable with those obtained with other ePADs (ranging

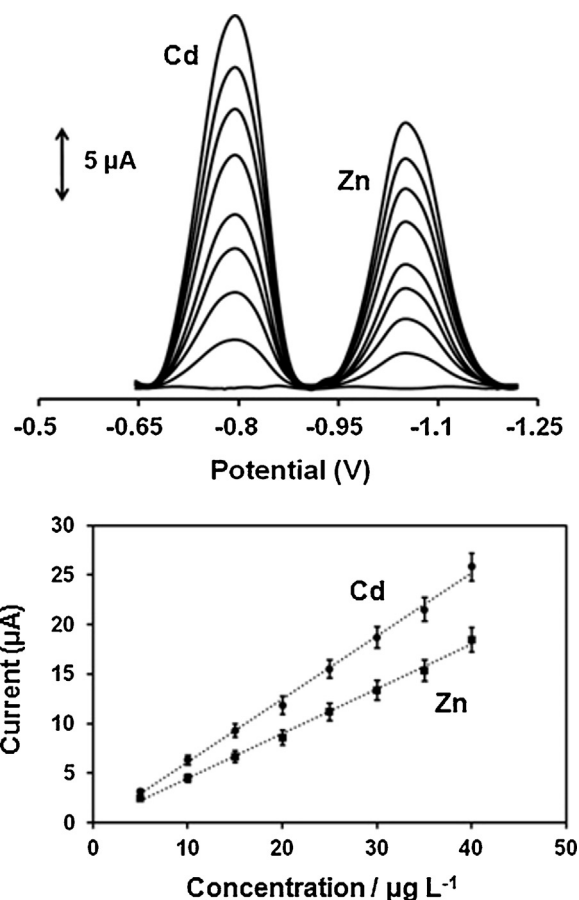


Fig. 3. Baseline-corrected SWASV voltammograms of 0 – $40 \mu\text{g L}^{-1}$ of Zn(II) and Cd(II) (in steps of $5 \mu\text{g L}^{-1}$) and the respective calibration plots. The error bars are the standard deviations for replicate measurements carried out at five ePADs.

from $0.2 \mu\text{g L}^{-1}$ to $25 \mu\text{g L}^{-1}$) [17,18]; so far, no ePADs have been reported to ASV determination of Zn(II). The between-sensor reproducibility (expressed as the % RSD at five different ePADs) was 5.7% for Cd(II) and 7.5% for Zn(II) at the $30 \mu\text{g L}^{-1}$ level. The effect of some possible interferences (Mn(II), Ni(II), Mg(II), Fe(III), Pb(II)) was also examined. The SWASV peaks of Cd(II) and Zn(II) at a concentration of $20 \mu\text{g L}^{-1}$ were not affected by 10-fold mass concentration excess of these cations. The well-known inference of Cu(II) can be alleviated by the addition of ferrocyanide or gallium ions as previously demonstrated [12]. Finally, the shelf-life of the sensors was tested over a period of 3 months using a Shewhart control chart. The SWASV response of the ePADs remained within the $\pm 2\text{SD}$ control limits (95% confidence level).

4. Conclusions

In this work, a new ePAD with integrated sputtered film electrodes (Sn (WE), Ag (RE), Pt (CE)) is described for the simultaneous ASV determination of Cd(II) and Zn(II). This ready-to-use ePAD presents significant advantages over conventional electrochemical ASV sensors and existing ePADs in terms of cost, scope for mass-production and simplicity of operation.

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