

Anodic Stripping Voltammetric Determination of Zinc at a 3-D Printed Carbon Nanofiber–Graphite–Polystyrene Electrode Using a Carbon Pseudo-Reference Electrode

Kevin C. Honeychurch¹, Zuhayr Rymansaib², and Pejman Iravani²

¹Centre for Research in Biosciences, Department of Applied Sciences, University of the West of England, Frenchay Campus, Coldharbour Lane, Bristol BS16 1QY, UK

²Department of Mechanical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, UK

Abstract

The application of a novel fully 3-D printed carbon nanofiber–graphite–polystyrene electrode has been investigated for the trace determination of Zn^{2+} by differential pulse anodic stripping voltammetry. The possibility of utilising a carbon pseudo-reference electrode was found to be successful. The effect of accumulation potential and time were investigated and optimised. Using an accumulation potential of -2.9 V (vs. C) and an accumulation time of 75 s a single sharp anodic stripping peak was recorded exhibiting a linear response from 12.7 $\mu\text{g/L}$ to 450 $\mu\text{g/L}$. The theoretical detection limit (3σ) was calculated as 8.6 $\mu\text{g/L}$. Using the optimised conditions a mean recovery of 97.8 %, (%CV = 2.0 %, $n = 5$) for a tap water sample fortified at 0.990 $\mu\text{g/mL}$ was obtained indicating the method holds promise for the determination of Zn^{2+} in such samples.

1. Introduction

Zinc is an essential element required for the activity of >300 enzymes [1]. It is required in a number of important industries and in a wide range of common household applications such as; batteries [2] and personal care products [3-5]. Demand for this metal is expected to increase as a result of reduced capacity, environmental policy constraints, closure of exhausted mines and from increased industrial demand [6]. One common application for Zn is in the alloy brass, used widely in plumbing and water systems. Concentrations of Zn leaching from plumbing fittings can result in a metallic or bitter taste that can sometimes occur in tap water. Consequently, the World Health Organisation

advises that drinking water containing Zn levels above 3 mg/L may not be acceptable to consumers and set standards for Zn in potable water vary from 1 mg/L in Japan to 5 mg/L in Canada and the USA [7] for this reason. Levels in tap water [8] and unpolluted environmental water [9] are generally much lower, in the $\mu\text{g/L}$ range, but in some instances levels as high as 6.7 mg/L [10] have been reported in rivers and elevated concentrations in rainwater collection tanks in the range of 1.1 and 10.8 mg/L have also been reported [11]. This is of possible concern, beyond that of taste issues, as studies have shown that elevated Zn levels in drinking water can be associated with type 1 diabetes in children [12].

Commonly, Zn is determined by atomic absorption spectrometry [13] and ICP-AES [14] or ICP-MS [15]. These approaches can be expensive, both in terms of infrastructure and resources [16] and in the requirement of highly trained staff for their application. However, electrochemical techniques such as stripping voltammetry have been shown to be both economic and sensitive and can be used by relatively untrained persons. Table 1 gives a summary of some recent applications of anodic stripping voltammetry (ASV) for the determination of Zn. The possibility of using ASV for the determination of Zn has been demonstrated using Hg based electrodes. However, the toxicity of Hg [17] has led to issues with its lack of acceptance in wide-scale routine analysis. Commonly, alternatives to Hg such as carbon working electrodes modified with either Bi [18] or Sb [19] have been employed for the stripping voltammetric determination of Zn and a number of metal ions [20]. Nevertheless, it has also been shown possible [21-24] to directly deposit the target metal analyte as a thin film directly on the carbon electrode itself.

One common technique that has been used to manufacture such carbon electrodes is screen-printing. This has become an increasingly common approach due to the large commercial application of screen-printed electrodes (SPEs) in the determination of blood glucose [25] and a number of SPEs based approaches have been developed for the determination of Zn [20]. Screen-printing requires well trained staff with an in-depth knowledge of the conditions required for

successful printing. Parameters such as; the type of solvent [26], binder [27], the condition of the squeegee [28] and curing temperature [29] can all lead to changes in the electrodes produced and their behaviour [30,31]. Investigations into improving their performance and reproducibility are commonly reported [32,33]. However, this can be problematic, as the composition of the carbon printing inks is generally proprietary information, resulting in a lack of knowledge of the structure of the printed electrode.

More recently, studies have shown the possibility of using the alternative technology of 3-D printing to fabricate carbon electrodes [34-40]. Unlike screen-printing, a considerable percentage of 3-D printing technology is presently based on the open-source model, facilitating the creative adaption of methods and for open sharing of expertise and innovation [41]. 3-D printing also has the advantages of allowing for the simple fabrication of new bespoke composite designs and other important sensor components, other than just the electrodes, such as micro-fluidic sample handling systems [42], analyte accumulation layers [43] and even whole electrochemical cells [42] to be fabricated using the same process, with the possibility of producing these with high precision utilising robotic printing techniques [44] having also been shown. 3-D printed carbon electrodes have been described for applications such as ECG monitoring [35] and for the detection of alkaline phosphatase via the chronoamperometric determination of *p*-nitrophenol [36]. However, these applications required multiple masking and patterning steps with PDMS and Au sputtering to give the finished device. As with the majority of previous applications of 3-D technology for electrode fabrication, these only use 3-D printing for part of the production process and ultimately still required further steps. Nevertheless, in a recent study [34], it has been shown possible to fabricate electrodes using 3-D-printing alone, without the need for further fabrication steps.

In this present study we have investigated the voltammetric behaviour of Zn at these newly designed and fully fabricated nanofiber 3-D printed carbon electrode initially as part of a conventional three electrode cell, using a saturated calomel reference electrode (SCE) and a carbon rod auxiliary

electrode. In the second section of our study we investigated the possibility of utilising this same 3-D printed working electrode as part of a novel all carbon electrochemical cell by using it in conjunction with a carbon pseudo-reference/counter electrode. In the final section we then investigated and optimised the conditions required for the differential pulse anodic stripping voltammetric (DPASV) determination of Zn in a fortified tap water sample.

Working electrode	Supporting electrolyte	Measurement technique	Linear range, $\mu\text{g/L}$	Detection limit, $\mu\text{g/L}$	Sample	Ref.
Ex situ deposited bismuth SPE	0.01 M KNO_3 and maleic/maleate buffer at pH 6.	DPASV, -1.5 V, 60 s. stripping chronopotentiometry	Up to: 250	3.5	Barcelona tap water	[45]
Bismuth oxide modified ink SPE	0.1 M sodium acetate solution containing 0.05 M HCl or 0.1 M HCl	SWASV, -1.2 V	40 - 150	30	River water	[46]
Hg thin film SPE	20 mM KH phthalate, 0.1 M MgCl_2	DPASV -1.4 (300 s)	10 - 500		--	[47]
Hg thin film SPE	120 mg/mL Hg_2Cl_2 , 20 mM potassium hydrogen phthalate, 0.1 MgCl_2	DPASV	Up to 1000	55.7	Water	[48]
In situ plated Bi SPE	0.1 M pH 4.5 acetate buffer, 10-2 M KCl	SWASV	10 – 100	8.2	Tap water and waste water	[49]
Hanging mercury drop electrode	0.1 M sodium acetate buffer at pH 6.5–7.0, and 1 μM Aluminon	Adsorptive cathodic stripping voltammetry	30 – 120	30	--	[50]
Hanging mercury drop electrode	4% (v/v) acetic acid solution	SWASV	Up to 200	0.5	Glazed ceramic surfaces	[51]
Glassy carbon electrode	Pyrophosphate (pH 4.0)	DPASV	100 – 400	14.7	Boiler feed water	[52]
Glassy carbon electrode	0.01 M acetate buffer solution (pH 4.6)	SWASV with the aid of sonication	13 – 65	6.5	Blood	[53]
3-D printed carbon electrode	0.1 M acetic acid	DPASV	12.7 – 450	8.6	Tap water	This study

Differential pulse anodic stripping voltammetry (DPASV), Screen-printed electrode (SPE), Square wave anodic stripping voltammetry (SWASV).

Table 1. Previously reported methods for the stripping voltammetric determination of zinc.

2. Experimental Section

2.1 Chemical and Reagents

Polystyrene pellets (441147), and graphite flakes (28286-3) were supplied by Sigma-Aldrich (Poole, UK). Acrylonitrile butadiene styrene (ABS) granules, MG94 resin were supplied by Sabic (OS3DP.com). High Impact Polystyrene (HIPS) filament (HIPS175W1) was obtained from CPC Farnell (Preston, UK) and Pyrograf III carbon nanofibers from Pyrograf Products, Inc. (pyrografproducts.com, PR-24-XT HHT).

Zinc stock solutions were prepared by dissolving the appropriate mass of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, Poole, UK) in deionised water. Working standards, for optimisation of studies, were prepared by dilution of the primary stock solution with deionised water. Deionised water was obtained from a Purite RO200–Stillplus HP System, (Purite Oxon, UK). Supporting electrolyte solutions for voltammetric studies were prepared by dilution of glacial acetic acid (Fisher, Loughborough, UK) to give a 0.1 M solution. **Acetate solutions** were made by mixing of acetic acid and sodium acetate (Fisher, Loughborough, UK) to give the desired pH.

2.2 Apparatus

Cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV) were performed with a Pstat10 potentiostat interfaced to a PC for data acquisition via the General Purpose Electrochemical System Software Package (GPES) version 3.4 (Autolab, Windsor Scientific Limited, Slough Berkshire UK). The cell used for the voltammetric measurements was obtained from Metrohm (Switzerland); a small magnetic stirrer bar was placed in the bottom of the cell for stirring in the pre-concentration step of DPASV. This was rotated at a fixed constant rate by a rotary stirrer (Mini MR Stirrer, Whatman, Maidstone, Kent, UK). All measurements were made using the 3-D printed working electrode with a graphite rod counter/pseudo-reference electrode. The 3-D printed working electrode was initially polished manually with slurries prepared from 50 μm aluminium

oxide on a smooth polishing mat. Residual polishing material was removed by rinsing with deionized water. The electrode was then repeatedly scanned using the cyclic voltammetric conditions described in section 2.4 until a constant background current was obtained.

2.3 Fabrication of Electrodes

2.3.1 Composite Thermoplastic Filament Fabrication

For a total 5 g of electrode conductor material, 4 g of polystyrene pellets are dissolved in 50 mL of chloroform and stirred with a magnetic stirrer until fully dissolved. The additives, 0.5 g of CNF and 0.5 g of graphite flakes are sonicated for 20 minutes in 50 mL of chloroform. Containers were sealed to prevent solvent evaporation. The two mixtures are then combined in a single open container and placed on a heated magnetic stirrer at 50 °C in a fume cupboard until all the solvent has evaporated. After the complete evaporation of the solvent, the solid thermoplastic composite is placed in a heated (220 °C) aluminium barrel with a 2 mm orifice and extruded into lengths of composite conductive filament to be used for 3D-printing.

2.3.2 Filament Characterization

Filament admittance measurements were carried out by pressing material into a disc, coating both sides with silver paint and analysing using a Solartron 1296 impedance analyser (UK). A 100 mV RMS AC signal is applied, sweeping from 1 Hz to 1 MHz. AC conductivity (admittance) is then calculated using eq. 1,

$$\sigma = \frac{Z'}{Z'^2 + Z''^2} \cdot \frac{t}{A} \quad (1)$$

where Z' and Z'' are the real and imaginary parts of the impedance, A is the area of the sample and t is the sample thickness. AC conductivity of the composite was thus evaluated to be 5.03 Sm^{-1} up to \approx

100 kHz.

2.3.3 CAD Design and 3D-Printing

The electrode was designed as a multi-material part using a CAD package (Solid Edge ST6). Electrode tip dimensions are 4.5 mm × 7.5 mm with a 0.81 mm × 0.81 mm active area in the centre (figure 1). The CAD file is subsequently processed with open source software Slic3r to convert to printing commands. A 350 µm layer height was used resulting in 9 layers for printing of the complete electrode. The electrodes were then printed using a custom-built fused filament deposition 3D-printer equipped with two 0.5 mm extruders.

2.4 Cyclic Voltammetry

Cyclic voltammograms were initially recorded with plain solutions of 0.1 M of the supporting electrolyte under investigation and then in the same solution containing 1.2 mM Zn. Degassing was achieved by purging with oxygen free nitrogen (BOC, Guildford, UK) for 5 minutes to eliminate oxygen reduction waves. A starting and final potential of 0.0 V was employed, with a switching potential of -2.5 V and a scan rate of 50 mV/s. A 3-D printed carbon working electrode with either a carbon pseudo-reference counter electrode or a saturated calomel reference electrode (SCE) and carbon rod counter electrode was employed.

2.5 Differential Pulse Anodic Stripping Voltammetry

Accumulation was carried out for 75 s at -2.9 V (vs. carbon). The stripping voltammogram was recorded using a differential pulse waveform using a step height of 10 mV, pulse repetition time 0.2 s, pulse amplitude of 50 mV, and pulse duration of 50 ms. The stripping voltammogram was recorded over the potential range -2.9 V to 0.0 V (vs. carbon). Degassing of the sample with nitrogen was found to be unnecessary.

2.6 Analytical Application

For evaluation of the method we determined Zn in a tap water sample collected from our laboratory, fortified to be 0.990 µg/mL using the following procedure. Aliquots (1.0 mL) of either unspiked tap water or tap water fortified to be 0.990 µg/mL of added Zn were transferred to the electrochemical cell and diluted to be 10 mL 0.1 M acetic acid. The concentration of Zn present was determined using the optimised DPASV conditions described. Quantification was performed using the method of multiple standard additions.

3. Results and Discussion

3.1 Cyclic Voltammetric Behaviour of Zinc

3.1.1 Effect of Supporting Electrolyte

Previous studies undertaken at carbon working electrodes have shown the importance of both the pH and the chemical nature of the supporting electrolyte [21,23]. A number of studies utilising carbon working electrodes have shown the advantages of acetate based supporting electrolytes [20]. Thus, in this present study we investigated 0.1 M acetate solutions at pH 3, 4, 5 and 6, and acetic acid itself as possible supporting electrolytes for the voltammetric determination of Zn²⁺. Cyclic voltammetric investigations showed that the largest oxidation peaks (figure 2) were obtained in 0.1 M acetic acid. Consequently, a 0.1 M acetic acid supporting electrolyte was used in further studies.

3.1.2 Carbon Auxiliary/Pseudo-Reference Electrode

Our initial DPASV investigations utilising a SCE as a reference electrode and a carbon auxiliary electrode were hampered by contamination of the supporting electrolyte with Zn²⁺ ions presumably diffusing from the internal salt solution of the saturated calomel reference electrode salt bridge [54]. To overcome this issue we investigated the possibility of utilising an alternative two electrode

carbon system. Previous investigations by Panzer and Elving [55] have demonstrated the possibility of utilising a carbon electrode as a reference electrode. It was critical to first demonstrate that this carbon counter/pseudo-reference electrode could provide stable electrochemical conditions during the accumulation and stripping steps of ASV. Thus, we assessed the suitability of our carbon counter/pseudo-reference electrode by investigating the cyclic voltammetric responses of a 1.2 mM Zn^{2+} solution in 0.1 M acetic acid supporting electrolyte (figure 3). The performance of the 3-D printed carbon electrode was investigated with both a conventional three electrode system (SCE and carbon counter electrode) and with a two electrode carbon counter/pseudo-reference. Our investigations showed the carbon based two electrode system overcame the problems of supporting electrolyte contamination and both peak currents (i_{pa}) (%CV = 4.50 %, n = 15) and peak potentials (E_p) (%CV = 2.60 %, n = 15) were highly reproducible. The voltammetric profiles were found to shift by approximately, 0.6 V but the overall behaviour of voltammogram was found to be very similar for both systems (figure 3). Consequently, the carbon counter/pseudo-reference system was utilised in further investigations.

3.2 Differential Pulse Anodic Stripping Voltammetry

As we were particularly interested in developing a method capable of determining trace levels of Zn^{2+} we elected to explore the possibility of utilising the more sensitive and selective differential pulse voltammetric waveform [21]. Figure 4 shows a typical differential pulse anodic stripping voltammogram obtained using an accumulation potential of -2.4 V (vs. C) and an accumulation time of 60 s for a 773.5 $\mu\text{g/L}$ (ppb) in a non-degassed solution. A well-defined stripping peak for Zn was obtained with a peak potential (E_p) of -1.8 V (vs. C). As this exhibited good analytical properties, we decided to explore this further.

3.2.1 Effect of Accumulation Potential

The Zn stripping peak was found to increase in magnitude as the accumulation potential was made more negative, and reached a maxima which became independent of accumulation potentials at

values more negative than -2.8 V (vs. C). Figure 5 shows the resulting plot of peak current vs. accumulation potential for a 773.5 µg/L Zn²⁺ 0.1 M acetic acid solution, using an accumulation time of 60 s. An accumulation potential of -2.9 V (vs. C) was hence used in further investigations. No evidence of hydrogen evolution was recorded at this potential.

3.2.2 Effect of Accumulation Time

The effect of accumulation time was studied over the range of 10 s to 80 s using a 773.5 µg/L Zn solution in 0.1 M acetic acid. Figure 6 shows a plot of deposition time vs. peak current. The peak current for the stripping peak increased linearly with accumulation times up to 75 s. At accumulation times greater than this the stripping peak became distorted and non-reproducible. We consequently decided to select a deposition time of 75 s for further studies.

3.2.4 Calibration Curve and Limit of Detection

A calibration study was carried out using Zn²⁺ standards prepared in 0.1 M acetic acid. These standards were subjected to DPASV using the optimised deposition time and deposition potentials values. Using an accumulation time of 75 s with an applied potential of -2.9 V (vs. C) a linear response was obtained from 12.7 µg/L to 450 µg/L with a slope of 3.552 nA/ng/mL ($R^2 = 0.999$) with a corresponding theoretical detection limit of 8.6 µg/L Zn (3σ). A coefficient of variation of 1.8 % was obtained for the determination of an 80.9 ng/mL Zn standard.

3.2.5 Interference Study

Investigations indicated that common ions found in tap water including nitrate, sulphate, chloride, sodium, calcium and magnesium did not interfere with the voltammetric determination of Zn (115 ng/mL) at molar ratios of (interferent : Zn²⁺) <75. As shown in Figure 7, 2:1 molar ratios of Cd²⁺, Pb²⁺ and Cu²⁺ were found to have no effect on the anodic stripping voltammetric response of Zn. Well defined stripping voltammetric peaks were also recorded for Cd, Pb and Cu. The formation of mono and multilayer stripping peaks commonly seen at solid electrodes are clearly observable for these

metals under the conditions employed. Both the peak shape and peak current of the Zn stripping peak remind unaffected by the presence of these three other metals demonstrating the possibility of using this approach in future studies for the simulations determination of all four metals.

4. Analytical Application

The 3-D printed carbon electrode was evaluated by carrying out Zn²⁺ determinations on a tap water sample. The deposition time and potential, as well as DPASV parameters were the same as used previously. The concentration of Zn²⁺ was determined using the method of multiple standard additions. The unfortified sample was found to contain 180 ng/mL Zn, similar levels to that reported in previous studies [8,23]. An aliquot (100 mL) of the sample was then fortified to be 0.990 µg/mL Zn and an aliquot (1.0 mL) added to the electrochemical cell. This was then diluted to be 10 mL 0.1 M acetic acid. The solution was then examined using the optimised DPASV method and a mean percentage recovery of 97.8 %, (n = 5, %CV = 2.0 %) was obtained. Figure 8 shows DPASVs of a representative fortified tap water sample.

5. Conclusions

A fully 3-D printed carbon working electrode has been successfully employed for the differential pulse voltammetric determination of trace concentrations of Zn²⁺ in water. The study shows that the fully 3-D printed nanocomposite electrodes exhibited good conductivity with low background currents and allowed for the formation of stable metal film formation essential for ASV. The electrode was found to be stable for at least a period of four months, with no special storage conditions being required. As previously noted [21], Zn can be a difficult element to determine by ASV as it deposits and stripping responses are often accompanied by hydrogen evolution at extreme negative potentials. However, our investigation as shown that trace levels of Zn could be readily determined by DPASV at our 3-D printed electrodes without the requirement to degas the sample or for the application of Bi, Hg or other metal films. Similar deposition and stripping characteristics

have been recorded to that seen at other carbon based electrodes [22,56]. The importance of both the nature of the supporting electrolyte and the deposition potential used have been shown to have notable effects on the nature of the stripping peaks recorded. It was shown possible to use this electrode as part of a carbon auxiliary/pseudo-reference two electrode system. This could offer a number of advantages overcoming contamination problems resulting from the components of the reference electrode and would in future studies allow for the possibility of 3-D printing the entire electrochemical cell; including the reference, counter and working electrodes. The performance characterises of the developed method compare well with those reported for other common electrode materials (table 1) such as SPE and Hg based electrodes and is better than that recently reported for the determination of Pb and Cd at a 3-D printed metal electrode [57].

6. Acknowledgements

We are grateful to the University of West of England, Bristol and the University of Bath for supporting our research. We are grateful to Prof. Frank Marken for his helpful discussions regarding the studies made here.

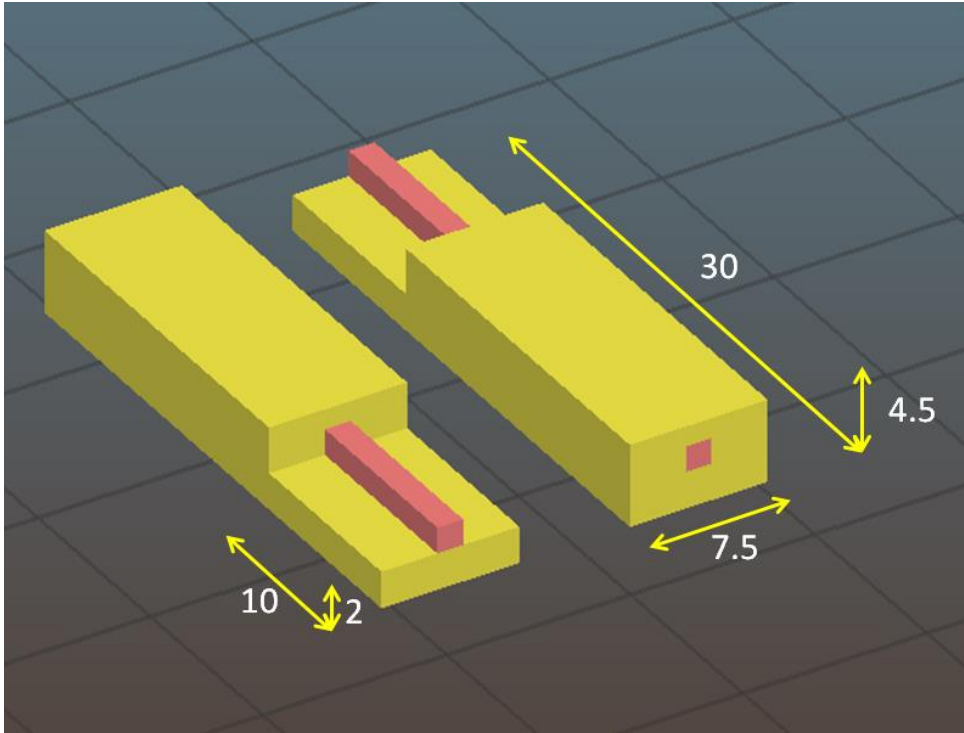


Figure 1. CAD image of electrode as shown in Slic3r software, annotated with part dimensions (mm)

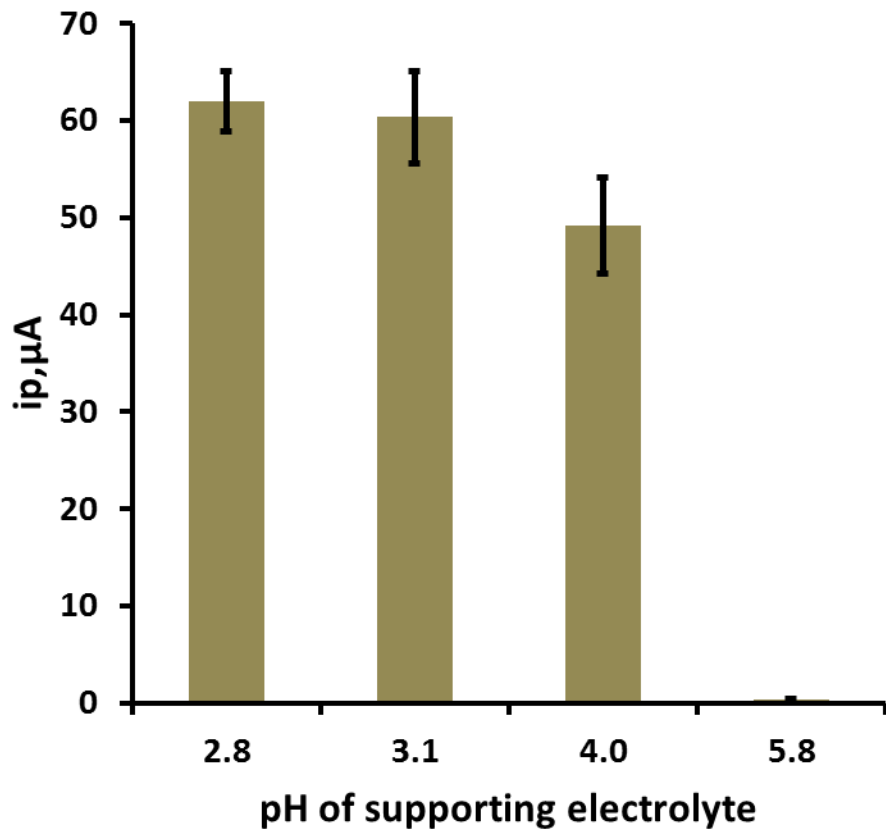


Figure 2. Effect of supporting electrolyte for a 1.2 mM Zn^{2+} 0.1 M supporting electrolyte solution.

Error bars represent $\pm\sigma$.

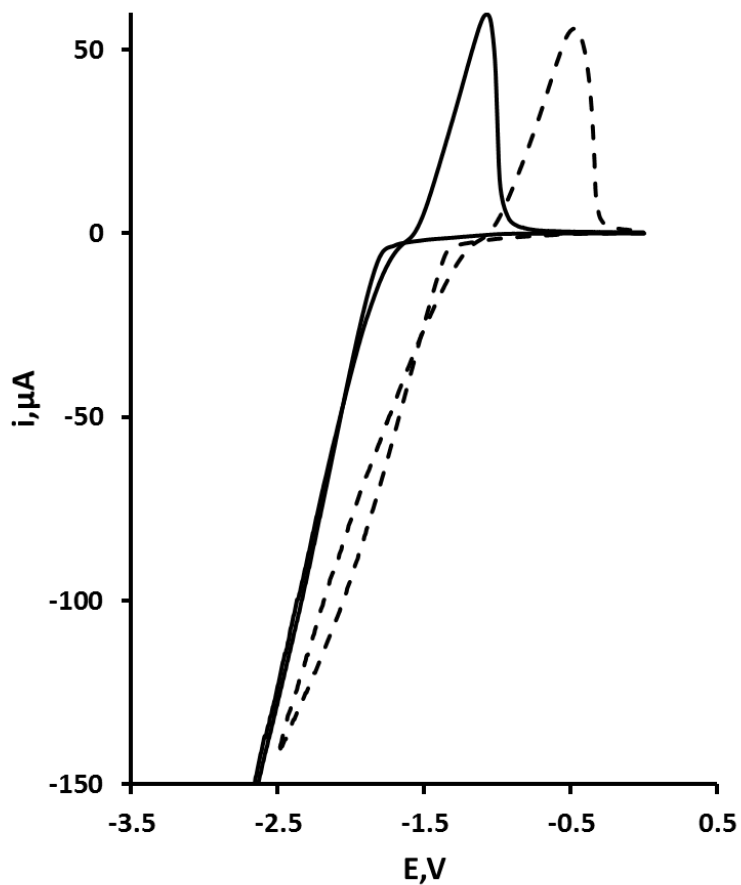


Figure 3. Cyclic voltammograms of 1.2 mM Zn^{2+} in 0.1 M acetic acid. Dashed line SCE reference; solid line carbon pseudo-reference electrode.

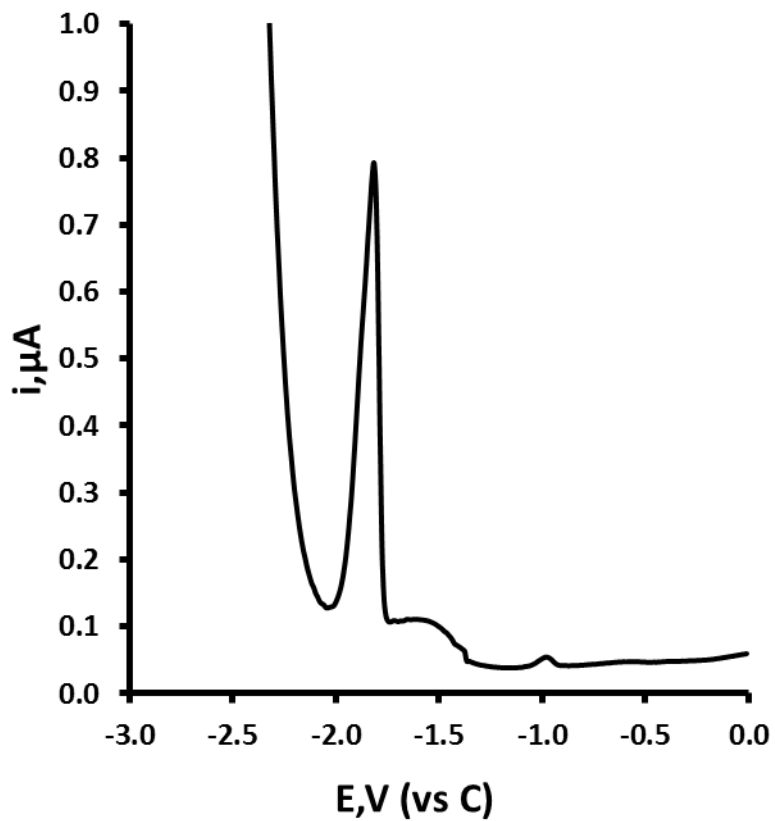


Figure 4. Typical differential pulse stripping voltammogram obtained for 773.5 $\mu\text{g/L Zn}^{2+}$ using an accumulation potential of -2.4 V and an accumulation time of 60 s.

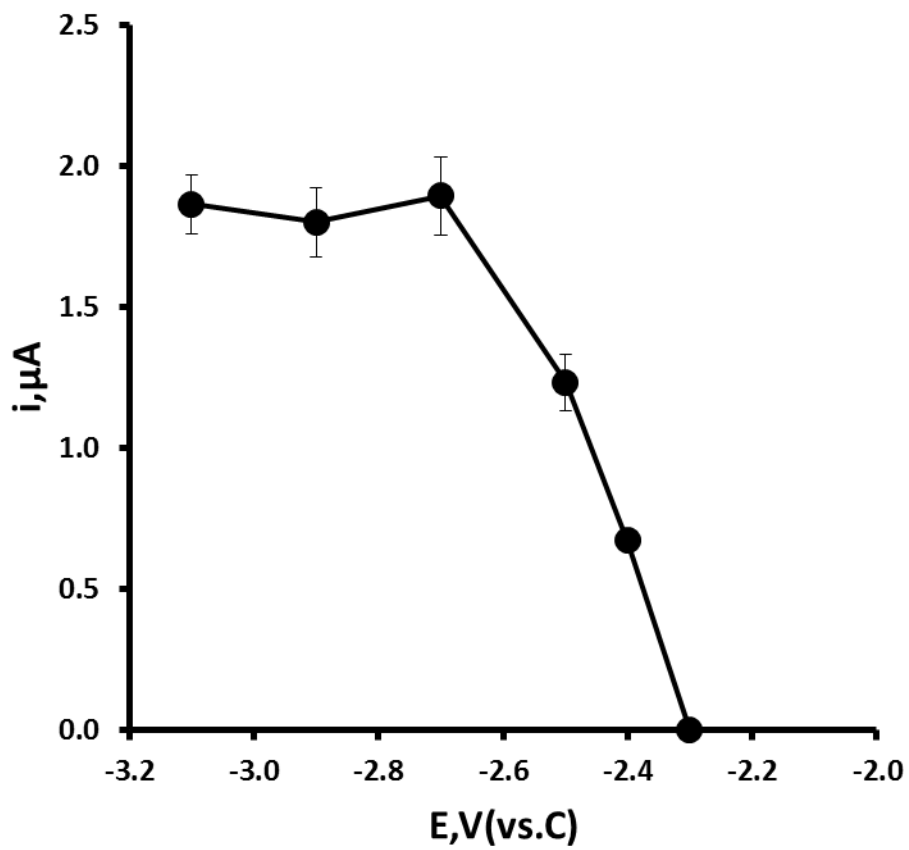


Figure 5. Effect of accumulation potential for a 773.5 $\mu\text{g/L Zn}^{2+}$ solution in 0.1 M acetic acid.

Accumulation time 75 s. Error bars represent $\pm\sigma$.

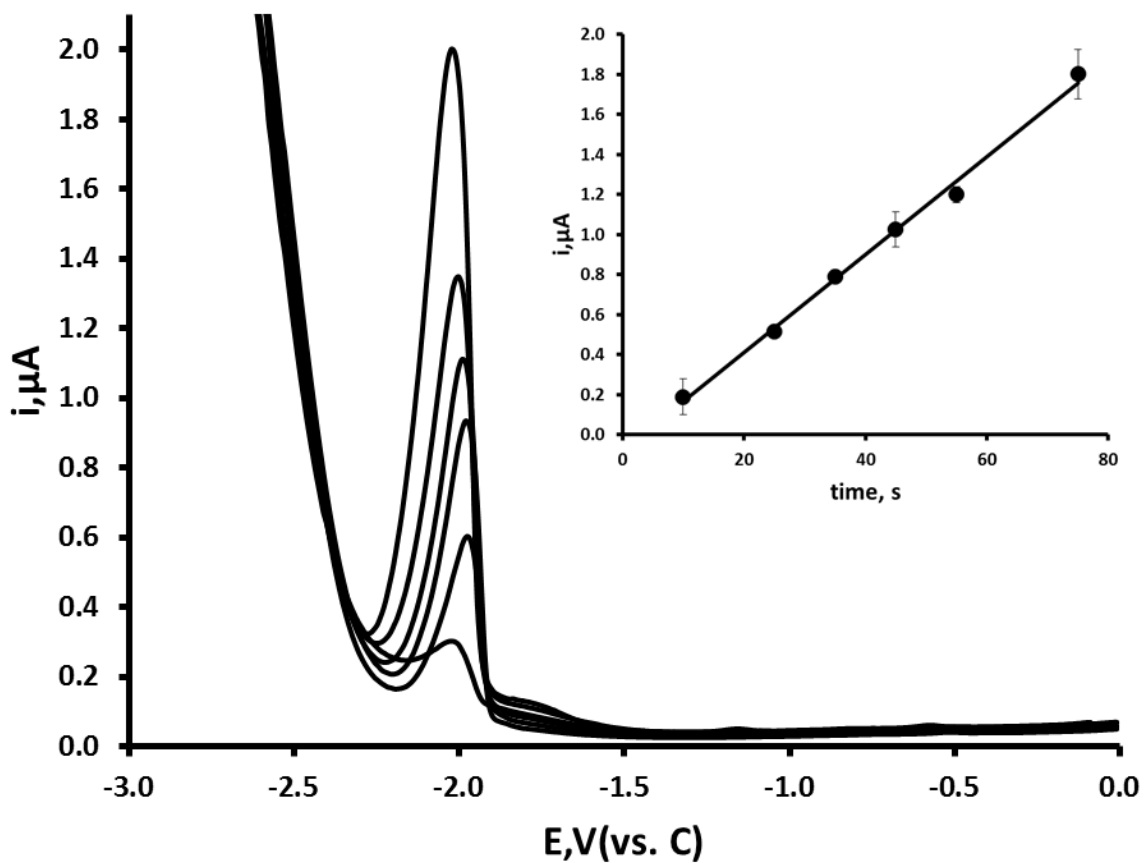


Figure 6. Effect of accumulation time on the magnitude of stripping peak current for 773.5 $\mu\text{g/L}$ Zn^{2+} . Accumulation potential -2.9 V (vs. C) and other conditions as Figure 4. Insert shows resulting plot of peak current vs. accumulation time. Error bars represent $\pm\sigma$.

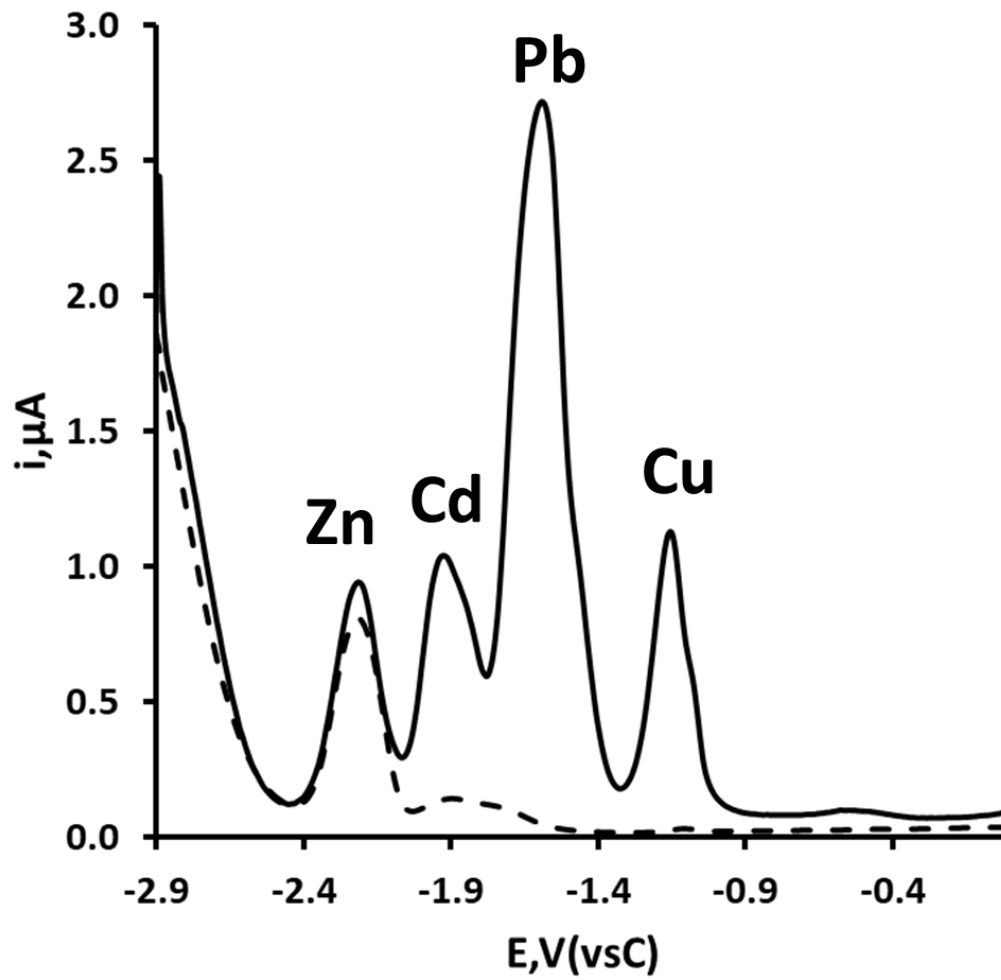


Figure 7. Anodic stripping voltammogram of 115 ng/mL Zn in absence of (dashed line) and in the presence of Pb, Cd and Cu (solid line) in 2:1 molar ratio.

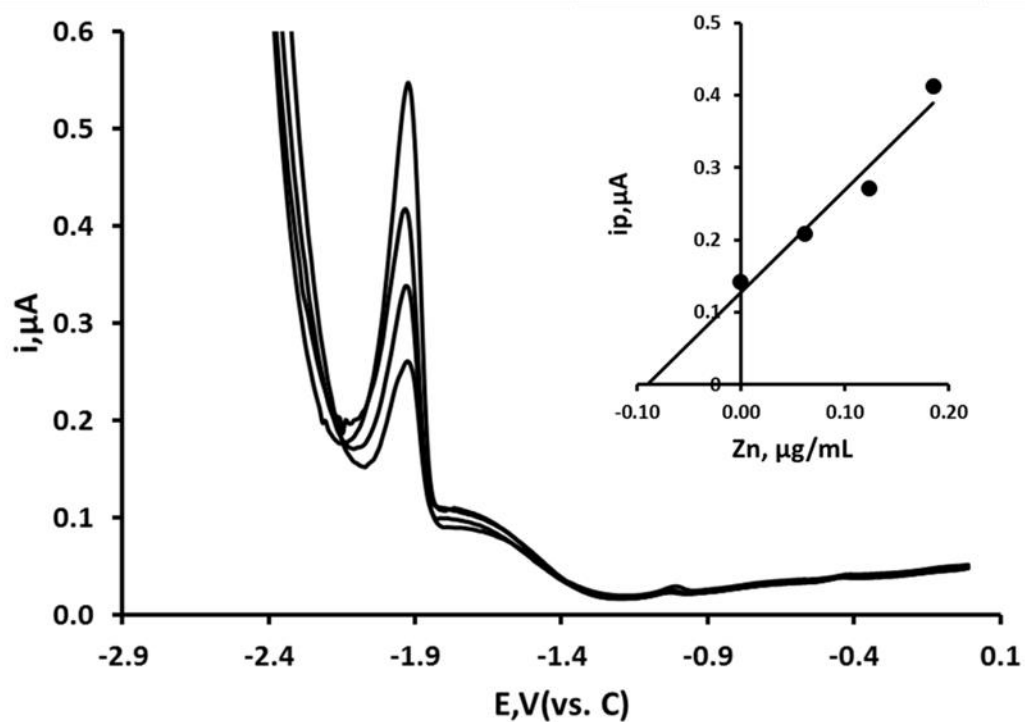


Figure 8. DPASVs of a representative tap water sample spiked with $0.990 \mu\text{g/mL Zn}^{2+}$ (diluted 10 times in 0.1 M acetic acid) with added concentrations of Zn^{2+} : 0 ng/mL; 61.8 ng/mL; 123.8 ng/mL; 185.6 ng/mL; Zn^{2+} added. Accumulation time: 75 s, deposition potential: -2.9 V (vs. C). Insert shows resulting standard addition plot for the fortified sample.

Figure and table legends

Figure 1. CAD image of electrode as shown in Slic3r software, annotated with part dimensions (mm)

Figure 2. Effect of supporting electrolyte for a 1.2 mM Zn^{2+} 0.1 M supporting electrolyte solution. Error bars represent $\pm\sigma$.

Figure 3. Cyclic voltammograms of 1.2 mM Zn^{2+} in 0.1 M acetic acid. Dashed line SCE reference; solid line carbon pseudo-reference electrode.

Figure 4. Typical differential pulse stripping voltammogram obtained for 773.5 $\mu\text{g/L}$ Zn^{2+} using an accumulation potential of -2.4 V and an accumulation time of 60 s.

Figure 5. Effect of accumulation potential for a 773.5 $\mu\text{g/L}$ Zn^{2+} solution in 0.1 M acetic acid. Accumulation time 75 s. Error bars represent $\pm\sigma$.

Figure 6. Effect of accumulation time on the magnitude of stripping peak current for 773.5 $\mu\text{g/L}$ Zn^{2+} . Accumulation potential -2.9 V (vs. C) and other conditions as Figure 4. Insert shows resulting plot of peak current vs. accumulation time. Error bars represent $\pm\sigma$.

Figure 7. Anodic stripping voltammogram of 115 ng/mL Zn in absence of (dashed line) and in the presence of Pb, Cd and Cu (solid line) in 2:1 molar ratio.

Figure 8. DPASVs of a representative tap water sample spiked with 0.990 $\mu\text{g/mL}$ Zn^{2+} (diluted 10 times in 0.1 M acetic acid) with added concentrations of Zn^{2+} : 0 ng/mL; 61.8 ng/mL; 123.8 ng/mL; 185.6 ng/mL; Zn^{2+} added. Accumulation time: 75 s, deposition potential: -2.9 V (vs. C). Insert shows resulting standard addition plot for the fortified sample.

7. References

- [1] K. A. McCall, C. -C. Huang, C. A. Fierke, Function and Mechanism of Zinc Metalloenzymes, *J. Nutr.* 130 (2000) 1437S.
- [2] J. -P. Wiaux, J. -P. Waefler, Recycling zinc batteries: an economical challenge in consumer waste, *J. Power Sources* 57 (1995) 61-65.
- [3] R. Marks, A. D. Pearse, A. P. Walker, The effects of a shampoo containing zinc pyrithione on the control of dandruff, *Br. J. Dermatol.* 112 (1985) 415-422.
- [4] S. Roldán, E. G. Winkel, D. Herrera, M. Sanz, A. J. Van Winkelhoff, The effects of a new mouthrinse containing chlorhexidine, cetylpyridinium chloride and zinc lactate on the microflora of oral halitosis patients: a dual-centre, double-blind placebo-controlled study, *J. Clin. Periodontol.* 30 (2003) 30, 427-434.
- [5] T. J. McCarthy, J. J. Zeelie, D. J. Krause, The antimicrobial action of zinc ion/antioxidant combinations. *Clin. Pharmacol. Ther.* 17 (1992) 51-54.
- [6] World Bank Group, Commodity Markets Outlook. From energy prices to food prices: Moving in tandem? A World Bank Quarterly Report, JULY 2016, Commodity Markets Outlook, July. World Bank, Washington, DC. License: Creative Commons Attribution CC BY 3.0 IGO <http://pubdocs.worldbank.org/en/328921469543025388/CMO-July-2016-Full-Report.pdf> accessed 23/10/16
- [7] D. Maycock, J. Fawell, G. Merrington, C. Watts, Review of England and Wales Monitoring Data for Which a National or International Standard Has Been Set (Defra Project Code: CEER 0703 DWI 70/2/215 WT1207) March 2008.
- [8] J. Raj, A. Raina, Mohineesh, T. D. Dogra, Direct Determination of Zinc, Cadmium, Lead, Copper Metal in Tap Water of Delhi (India) by Anodic Stripping Voltammetry Technique, E3S Web of Conferences 2013, doi.org/10.1051/e3sconf/20130109009
- [9] C. Terrés-Martos, M. Navarro-Alarcón, F. Martín-Lagos, R. Giménez-Martínez, H. López-García De La Serrana, M. C. López-Martínez, Determination of zinc levels in waters from southeastern Spain by electrothermal atomic absorption spectrometry: relationship with industrial activity, *Water Res.* 36 (2002) 1912-1916.
- [10] A. J. Sayyed, B. A. Bhosle, The study of zinc metal concentration by spectrophotometric method from Godavari River at Nanded, Maharashtra, *Der Chemica Sinica*, 1 (2010) 104-109.
- [11] B. Gulson, M. Korsch, A. Bradshaw, Impact of Dust from Ore Processing Facilities on Rain Water Collection Tanks in a Tropical Environment—The Obvious Source “Ain’t Necessarily So”, *Int. J. Environ. Res. Public Health*, 13 (2016) 243.
- [12] H. X. Zhao, M. D. Mold, E. A. Stenhouse, S. C. Bird, D. E. Wright, A. G. Demaine, B. A. Millward, Drinking water composition and childhood onset Type 1 diabetes mellitus in Devon and Cornwall, England, *Diabet. Med.* 18 (2001) 709-717.
- [13] S. P. Han, W. E. Gan, Q. D. Su, On-line sample digestion using an electromagnetic heating column for the determination of zinc and manganese in tea leaf by flame atomic absorption spectrometry, *Talanta* 72 (2007) 1481-1486.
- [14] D. Baralkiewicz, A. Hanc, H. Gramowska, Simultaneous determination of Cd, Cr, Cu, Ni, Pb and Zn in sewage sludge by slurry introduction ICP-OES method, *Int. J. Environ. Anal. Chem.* 90 (2010) 1025-1035.
- [15] C. Sariego Muñiz, J. M. Marchante Gayón, J. Ignacio García Alonso, A. Sanz-Medel, Accurate determination of iron, copper and zinc in human serum by isotope dilution analysis using double focusing ICP-MS, *J. Anal. At. Spectrom.* 14 (1999) 1505-1510.
- [16] R. R. Brooks, M. Hoashi, S. M. Wilson, R. -Q. Zhang, Extraction into methyl isobutyl ketone of metal complexes with ammonium pyrrolidine dithiocarbamate formed in strongly acidic media, *Anal. Chim. Acta*, 217 (1989) 165-170.

- [17] E. Gustafsson, Swedish experiences of the ban on products containing mercury, *Water Air Soil Pollut.* 80 (1995) 99-102.
- [18] J. Wang, J. Lua, Ü. A. Kirgöz, S. B. Hocevar, B. Ogorevc, Insights into the anodic stripping voltammetric behavior of bismuth film electrodes, *Anal. Chim. Acta*, 434 (2001) 29-34.
- [19] S. B. Hocevar, I. Švancara, B. Ogorevc, K. Vytřas, Antimony Film Electrode for Electrochemical Stripping Analysis, *Anal. Chem.* 79 (2007) 8639-8643.
- [20] K. C. Honeychurch, Screen-printed electrochemical sensors and biosensors for monitoring metal pollutants. *Insciences J.* 2 (2012) 1-51.
- [21] N. van Dijk, S. Fletcher, C. E. Madden, F. Marken, Nanocomposite electrodes made of carbon nanofibers and black wax. Anodic stripping voltammetry of zinc and lead, *Analyst*, 126 (2001) 1878-1881.
- [22] K. C. Honeychurch, J. P. Hart, D. C. Cowell, Voltammetric behavior and trace determination of lead at a mercury-free screen-printed carbon electrode, *Electroanalysis*, 12 (2000) 171-177.
- [23] S. Yilmaz, S. Yagmur, G. Saglikoglu, M. Sadikoglu, Direct Determination of Zn Heavy Metal in Tap Water of Canakkale (TURKEY) by Anodic Stripping Voltammetry Technique, *Int. J. Electrochem. Sci.* 4 (2009) 288-294.
- [24] K. C. Honeychurch, D. M. Hawkins, J. P. Hart, D. C. Cowell, Voltammetric behaviour and trace determination of copper at a mercury-free screen-printed carbon electrode, *Talanta*, 57 (2002) 565-574.
- [25] K. C. Honeychurch, *Thick-film biosensors*. In: Prudenziati, M. and Hormadaly, J., eds. 2012 *Printed Films Materials Science and Applications in Sensors Electronics and Photonics*. 1. UK: Woodhead Publishing.
- [26] E. H. Jewell, T. C. Claypole, D. T. Gethin, Viscosity control in the screen printing of ceramic transfers. *Surf. Coat. Int. Part B Coat. Trans.* 86 (2003) 155-163.
- [27] N. A. Choudhry, D. K. Kampouris, R. O. Kadara, N. Jenkinson, C. E. Banks, Next generation screen printed electrochemical platforms: Non-enzymatic sensing of carbohydrates using copper (ii) oxide screen printed electrodes. *Anal. Methods* 1 (2009) 183-187.
- [28] E. H. Jewell, T. C. Claypole, D. T. Gethin, The effect of exposure to inks and solvents on squeegee performance. *Surf. Coat. Int. Part B Coat. Trans.* 87 (2004) 253-260.
- [29] K. Grennan, A. J. Killard, M. R. Smyth, Physical characterization of a screen-printed electrode for use in an amperometric biosensor system. *Electroanalysis*, 13 (2001) 745-750.
- [30] Y. Wang, E. Laborda, R. G. Compton, Electrochemical oxidation of nitrite: Kinetic, mechanistic and analytical study by square wave voltammetry, *J. Electroanal. Chem.* 670 (2012) 56-61.
- [31] C. W. Foster, R. O. Kadara, C. E. Banks, *Fundamentals of Screen-Printing Electrochemical Architectures*, in C. W. Foster, R. O. Kadara, C. E. Banks, *Screen-Printing Electrochemical Architectures*, chapter 2, Part of the series Springer Briefs in Applied Sciences and Technology pp. 13-23, 2015.
- [32] L. R. Cumba, C. W. Foster, D.A.C. Brownson, J. P. Smith, J. Iniesta, B. Thakur, D. R. do Carmo, C.E. Banks, Can the mechanical activation (polishing) of screen-printed electrodes enhance their electroanalytical response? *Analyst*, 141 (2016) 2791-2799.
- [33] M. Pravda, C. G. O'Meara, G. Guilbault, Polishing of screen-printed electrodes improves IgG adsorption, *Talanta* 54 (2001) 887-892.
- [34] Z. Rymansaib, P. Irvani, E. Emslie, M. Medvidovic-Kosanovic, M. Sak-Borsnar, R. Verdejo, F. Marken, All-Polystyrene 3D-Printed Electrochemical Device with Embedded Carbon Nanofiber – Graphite – Polystyrene Composite Conductor, *Electroanalysis*, 28 (2016) 28, 1517-1523.
- [35] P. Salvoa, R. Raedt, E. Carrette, D. Schaubroeck, J. Vanfleteren, L. Cardon, A 3D printed dry electrode for ECG/EEG recording, *Sens. Actuators A Phys.* 174 (2012) 96-102.

- [36] Y. Djafari, N. Abolfathi, An inexpensive 3D printed amperometric oxygen sensor for transcutaneous oxygen monitoring, 2017, 2016 23rd Iranian Conference on Biomedical Engineering and 2016 1st International Iranian Conference on Biomedical Engineering, ICBME 2016 7890972, pp. 281-284.
- [37] M. Pohanka, Three-Dimensional Printing in Analytical Chemistry: Principles and Applications, *Anal. Lett.* 49 (2016) 2865-2882.
- [38] A. Ambrosi, M. Pumera, 3D-printing technologies for electrochemical applications, *Chem. Soc. Rev.* 45 (2016) 2740-2755.
- [39] A. H. Loo, C. K. Chua, M. Pumera, DNA biosensing with 3D printing technology, *Analyst*, 142 (2017) 279-283.
- [40] H. Ragonés, D. Schreiber, A. Inberg, O. Berkh, G. Kósa, A. Freeman, Y. Shacham-Diamand, Disposable electrochemical sensor prepared using 3D printing for cell and tissue diagnostics, *Sens. Actuator B-Chem.* 216 (2015) 434-442.
- [41] P. J. Kitson, S. Glatzel, W. Chen, C. -G. Lin, Y. -F. Song, L. Cronin, 3D printing of versatile reactionware for chemical synthesis, *Nat. Protoc.* 11 (2016) 920-936.
- [42] B. Gross, S. Y. Lockwood, D. M. Spence, Recent Advances in Analytical Chemistry by 3D Printing, *Anal. Chem.* 89 (2017) 57-70.
- [43] C. -K. Su, P. -J. Peng, Y. -C. Sun, Fully 3D-Printed Preconcentrator for Selective Extraction of Trace Elements in Seawater, *Anal. Chem.* 87 (2015) 6945-6950.
- [44] R. Jones, P. Haufe, E. Sells, P. Iravani, V. Olliver, C. Palmer, A. Bowyer, RepRap—the replicating rapid prototype, *Robotica*, 29 (2011) 177-191.
- [45] N. Serrano, J. M. Díaz-Cruz, C. Ariño, M. Esteban, Stripping analysis of heavy metals in tap water using the bismuth film electrode. *Anal. Bioanal. Chem.* 396 (2010) 1365-1369.
- [46] R. O. Kadara, N. Jenkinson, C. E. Banks, Disposable Bismuth Oxide Screen Printed Electrodes for the High Throughput Screening of Heavy Metals. *Electroanalysis*, 21 (2009) 2410-2414.
- [47] D. Desmond, B. Lane, J. Alderman, G. Hall, M. Alvarez-leaza, A. Garde, J. Ryan, L. Barry, G. Svehla, D. W. M. Arrigan, L. Schniffner, An ASIC-based system for stripping voltammetric determination of trace metals. *Sensor. Actuat. B-Chem.* B34 (1996) 466-470.
- [48] D. Desmond, B. Lane, J. Alderman, G. Hall, D. W. M. Arrigan, J. D. Glennon, An environmental monitoring system for trace metals using stripping voltammetry. *Sensor. Actuat. B-Chem.*, B48 (1998) 409-414.
- [49] M. A. G. Rico, M. Olivares-Marin, E. P. Gil, A Novel Cell Design for the Improved Stripping Voltammetric Detection of Zn(II), Cd(II), and Pb(II) on Commercial Screen-Printed Strips by Bismuth Codeposition in Stirred Solutions. *Electroanalysis*, 20 (2008) 2608-2613.
- [50] K. -W. Cha, C. Park, S. -H. Park, Simultaneous determination of trace uranium(VI) and zinc(II) by adsorptive cathodic stripping voltammetry with aluminon ligand, *Talanta* 52 (2000) 983.
- [51] J. Jakmuneea, J. Junsomboona, Determination of cadmium, lead, copper and zinc in the acetic acid extract of glazed ceramic surfaces by anodic stripping voltammetric method, *Talanta* 77 (2008) 172-175.
- [52] J. F. van Staden, M. C. Matoetoe, Simultaneous determination of copper, lead, cadmium and zinc using differential pulse anodic stripping voltammetry in a flow system, *Anal. Chim. Acta* 411 (2000) 201-207.
- [53] J. Kruusma, C. E. Banks, L. Nei, R. G. Compton, Electroanalytical detection of zinc in whole blood, *Anal. Chim. Acta* 510 (2004) 85-90.
- [54] A. W. Bott, Practical Problems in Voltammetry 3: Reference Electrodes for Voltammetry, *Curr. Sep.* 14 (1995) 64-68.
- [55] R. E. Panzer, P. J. Elving, Nature of the surface compounds and reactions observed on graphite electrodes, *Electrochim. Acta* 20 (1975) 611-647.
- [56] J. T. Byrne, N. K. Rogers, Critical Interpretation of Electrodeposition Studies Involving Traces of Elements, *J. Electrochem. Soc.* 98 (1951) 457-463.

- [57] K. Y. Lee, A. Ambrosi, M. Pumera, 3D-printed Metal Electrodes for Heavy Metals Detection by Anodic Stripping Voltammetry, *Electroanalysis* 29 (2017) 2444-2453.