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# The Voltammetric Behaviour of Lead at a Hand Drawn Pencil Electrode and Its Trace Determination in Water by Stripping Voltammetry

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## Abstract

This is the first reported the proof of concept application of pencil drawn electrodes (PDEs) for anodic stripping voltammetric determination of  $\text{Pb}^{2+}$  or any metal ion. PDEs offer advantages of economics, simplicity and rapid fabrication, affording a green alternative for the development of new devices. Cyclic voltammetric investigations of  $\text{Pb}^{2+}$  at these electrodes in 0.30 M acetic acid were characterised by a cathodic reduction peak on the initial negative scan resulting from the reduction of  $\text{Pb}^{2+}$  ions to  $\text{Pb}^0$ . Anodic peaks obtained on the return positive scan showed that Pb had been deposited as a thin film on the PDE surface. The addition of  $\text{Cl}^-$  ions to this electrolyte improved the voltammetric behaviour and a supporting electrolyte of 0.30 M acetic acid containing 0.25 M KCl was found to be optimum. Investigations were made into the possibility of determining trace levels of  $\text{Pb}^{2+}$  by differential pulse anodic stripping voltammetry. The effect of accumulation potential and time were investigated and optimised. Three anodic stripping peaks were recorded resulting from the heterogeneous nature of the electrode surface. Using an accumulation potential of -1.1 V and an accumulation time of 200 s a bimodal calibration curve was recorded, with linear ranges between 80 to 330 ng/mL and 330 to 915 ng/mL. The theoretical detection limit ( $3\sigma$ ) was calculated as 9.5 ng/mL.  $\text{Pb}^{2+}$  determinations on a drainage water sample gave a mean recovery of 100.9 % (%CV= 5.7 %) at a concentration of 166.1 ng/mL indicating the method holds promise for the determination of  $\text{Pb}^{2+}$  in such samples.

## Introduction

Carbon electrodes have are widely used in electrochemistry and are a well-established technology [1]. A number of different carbon based materials and technologies have been commonly utilised such as glassy carbon [2], carbon paste [3] or screen-printed [4]. All of these approaches require some degree of expertise, preparation and care. As a result, a number of alternative sources for the manufacture of carbon electrodes have been investigated, such as the utilisation of pencil leads as electrodes [5-12]. The pencil "lead" is actually a mixture of graphite, wax and clay, the proportions of which impart different properties to the pencil with increasing amounts of clay making the pencil harder, hence the designation 'H'. Increasing the levels of graphite make the pencil softer, and their marks darker or black and so the designation 'B'. For example, one of the darkest generally available pencils, the 6B is 84 % graphite, 10 % clay and 5 % wax, compared to the common, lighter HB, or No. 2 pencil which has a composition of 68 % graphite, 26 % clay and 5 % wax [13]. Commonly, pencils have been used directly as the working electrode itself [5-12], only recently has the possibility of using pencils to draw electrodes and other electronic components onto a suitable substrate been reported [14]. This latter approach has a number of advantages, as designs and geometries can be easily altered as they are simply drawn by hand on to a suitable substrate. This allows for an extremely facile, green, low-cost, rapid method to fabricate electrode prototypes, as illustrated in table 1.

A number of different electrochemical applications including resistors, capacitors, UV and piezoresistive sensors, microfluidic devices, chemiresistive sensors, biosensors, batteries and field effect transistors have been reported [14]. However, there have only been a small number of reports on the application of these devices using voltammetry and until now its application has been generally only in the characterisation of the electrode [15]. Recently, Santhiago and Kubota [16] have developed a glucose biosensor employing paper and a pencil drawn working electrode modified with the mediator 4-aminophenylboronic acid and glucose oxidase (GOD). Hydrogen peroxide formed during the enzymatic reaction of glucose resulted in the oxidation of 4-aminophenylboronic acid to 4-aminophenol which was determined voltammetrically at the Pencil drawn electrode (PDE). Dossi *et al* [17] have also explored the electrochemical behaviour of ascorbic acid, dopamine and paracetamol

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3 by cyclic voltammetry at their PDEs and have reported well-defined redox behaviour. Thin-layer  
4 chromatography was used to separate mixtures of these compounds and co-eluting species could be  
5 identified using a dual electrode redox system formed from two in series PDEs. Recently, Santhiago  
6 *et al* [18] have used a 6B pencil to draw a counter electrode as part of a three electrode system for the  
7 voltammetric determination of *p*-nitrophenol. However, the system used a pencil lead as the working  
8 electrode.

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11 This present study investigates the possibility of using PDEs for the anodic stripping voltammetric  
12 (ASV) determination of Pb. This is believed to be the first reported application for such devices for  
13 the stripping voltammetric determination of Pb<sup>2+</sup> or any other metal ion. The toxicity of Pb is widely  
14 understood, causing a wide range of different conditions, such as: reduced birth weight, vitamin D  
15 metabolism interference, learning difficulties [19], reduction in IQ [20], increased hearing threshold  
16 [21], hypertension [22,23] and decreased sperm counts [24] and possible mutagenic effects [25].  
17 Lead is also increasingly implicated in dementia in the elderly [26] as levels stored in bone are  
18 released into the body due to processes associated with osteoporosis. A link has also been drawn with  
19 the levels of violence and antisocial behaviour in society [27,28]. As a result, a number of different  
20 measures have been undertaken to lower our exposure, such as its removal from petrol, paint and  
21 plumbing. Nevertheless, there are still a number of issues with the previous usage of Pb resulting in a  
22 legacy of widespread contamination [29]. Present day Pb blood levels are still between 50 to 200  
23 times greater than the blood Pb concentrations of preindustrial humans at about 0.8 nM (0.016 µg/dL)  
24 [30-32]. Advances in toxicology have highlighted the increasingly smaller concentrations that Pb is  
25 known to cause adverse effects [33,34]. This has shown levels previously thought to be acceptable to  
26 be too high. Consequently, there is pressing need to monitor Pb levels in a range of media. A number  
27 of different analytical methods have been utilised, including inductively coupled plasma [35] and  
28 atomic adsorption spectroscopy [36], requiring well equipped laboratories, refined gases and high  
29 electrical power consumption for their implementation. Electrochemical techniques have been  
30 highlighted [4,37] as an alternative method offering a number of advantages. Modern handheld  
31 instruments requiring little more than an appropriate power supply and can be even operated under  
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battery power alone. One such electrochemical technique, anodic stripping voltammetry, has been shown to be able to gain the low detection limits required [37]. The sensitivity of the assay can be tailored by altering the length of the accumulation step. Short accumulation times, in the order of less than one minute, can be used to determine sub to high ppm levels, with ppb and even sub ppb levels can be determined if the accumulation time is extended.

The aim of this present study was to investigate the possibility of using PDEs for the anodic stripping voltammetric determination of trace concentrations of Pb. The voltammetric behaviour of Pb at the electrode was first investigated by cyclic voltammetry. The optimum conditions required for the stripping voltammetric determination of Pb were then identified and finally the possibility of determining trace levels of Pb in environmental surface waters was explored.

Analyte	Fabrication	Analytical Technique	Reference
Glucose	Pencil drawn working electrode with a Ag ink pseudo-reference/counter electrode.	Glucose biosensor. Working electrode modified with the mediator; 4-aminophenylboronic acid and glucose oxidase. Voltammetric determination of enzymatically generated 4-aminophenol	[16]
Ascorbic acid, dopamine and paracetamol	Pencil drawn dual electrode	Thin-layer chromatography used to separate compound mixtures. Co-eluting species could be identified using dual electrode redox system	[17]
<i>p</i> -nitrophenol	A 6B pencil drawn counter electrode	Counter electrode as part of a three electrode system with pencil working electrode	[18]
Toluene, THF, ethyl acetate, methanol, hexane to acetone	Chemiresistors hand-drawn on paper	Solvent vapour measured at pencil drawn Chemiresistor	[38]
Mechanical strain	Chemiresistors hand-drawn on paper	Output voltage for an HB pencil was found to be more sensitive than that for a 9B pencil	[39]
Cysteine and hydrogen	Doped pencil leads for drawing modified electrodes	Cysteine and hydrogen peroxide linear range 0.5–	[40]

peroxide	on paper. Carbon pencil leads doped with either decamethylferrocene or cobalt (II) phthalocyanine	10 mM at cobalt (II) phthalocyanine modified pencil drawn electrode	
Hexacyanoferrate (II) and 1,2-hydroxybenzene	Pencil leads doped with Ag and AgCl drawn on paper to from Ag/AgCl reference electrodes	Performance evaluated by voltammetric measurements of hexacyanoferrate(II) and 1,2-hydroxybenzene as probe species	[41]
Carbohydrate antigen 199	Entirely hand drawn with commercially available crayon and pencils	Linear response range from 0.01–200 U/mL. Detection limit of 0.0055 U/mL obtained by electrochemiluminescence	[42]
Lead	6B pencil drawn carbon electrode	Anodic stripping voltammetry	This work

**Table 1. Recent applications of pencil drawn electrodes.**

## Experimental Section

### Chemical and Reagents

All chemicals were supplied from Fisher (Loughborough, UK), unless otherwise stated. Lead stock solutions were prepared by dissolving the appropriate mass of  $\text{Pb}(\text{NO}_3)_2$  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). Electrolyte solutions for cyclic voltammetric studies were prepared by dilution of glacial acetic acid to give a 0.30 M solution. This was then fortified with sufficient KCl to give a 0.25 M solution. Environmental water samples were obtained from a rainwater drainage ditch from the Frenchay Campus of the University of the West of England, UK.

### Fabrication of Pencil Drawn Sensors

The sensor was fabricated by drawing of the electrode design onto a 0.5 mm PVC substrate (Cadillac Plastics, Swindon, UK) with a 6B pencil (Derwent Graphic, UK). A 4 mm diameter working electrode was drawn with a 10 mm x 2 mm connection strip. The working electrode area was defined with dielectric tape (RS Components, Corby, Northamptonshire, UK). The working electrode was then cut from the PVC support and the connecting strip trimmed to 10 mm. The electrode was then

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3 connected to the potentiostat using a gold clip attached to coaxial cable inserted into the appropriate  
4 sockets.  
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### 7 8 **Apparatus**

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10 Cyclic voltammetry, linear sweep anodic stripping voltammetry (LSASV) and differential pulse  
11 anodic stripping voltammetry (DPASV) were performed with a Pstat10 potentiostat interfaced to a PC  
12 for data acquisition via the General Purpose Electrochemical System Software Package (GPES)  
13 version 3.4 (Autolab, Windsor Scientific Limited, Slough Berkshire UK). The cell used for the  
14 voltammetric measurements was obtained from Metrohm (Switzerland); a small magnetic stirrer bar  
15 was placed in the bottom of the cell for stirring in the pre-concentration step of DPASV. This was  
16 rotated at a fixed constant rate by a rotary stirrer (Mini MR Stirrer, Whatman, Maidstone, Kent, UK).  
17 All measurements were made using the PDE was the working with a saturated calomel reference  
18 (Russell, UK) electrode and a graphite rod counter electrode.  
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### 29 **Cyclic voltammetry**

30 Cyclic voltammograms were initially recorded with plain solutions of 0.30 M acetic acid, containing  
31 0.25 M KCl and then in the same solution containing 0.1 mM Pb. Degassing was achieved by  
32 purging with oxygen free nitrogen (BOC, Guildford, UK) for 5 minutes to eliminate oxygen reduction  
33 waves. A starting and end potential of 0.0 V (*vs.* SCE) was used, with a switching potential of  $-1.5$  V  
34 (*vs.* SCE) and a scan rate of 50 mV/s.  
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### 42 **Differential Pulse Anodic Stripping Voltammetry**

43 Accumulation was carried out for 200 s at  $-1.1$  V (*vs.* SCE). Initially, the stripping voltammogram  
44 was recorded using linear sweep voltammetry using a scan rate of 50 mV/s. Further studies were  
45 made by DPASV using a step height of 10 mV, pulse repetition time 0.2 s, pulse amplitude of 50 mV,  
46 and pulse duration of 50 ms. The stripping voltammogram was recorded over the potential range  $-1.1$   
47 V to 0.0 V (*vs.* SCE).  
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### 55 **Scanning Electron Microscopy**

56 Scanning electron microscopy was undertaken using a Philips XL30 ESEM system.  
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## Results

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) (Figure 1) investigations showed the surface of the PDE to be heterogeneous in nature showing good coverage of the underlying PVC substrate. The topography of the electrode surface would seem to follow the underlying PVC substrate. This is similar to that seen by Lin *et al* [38] in studies undertaken on paper substrates. Further investigations showed a mean resistance of 1.9 k $\Omega$  (%CV = 2.53 %) was obtained for ten PDEs.

### Cyclic Voltammetry

Figure 2 shows a typical cyclic voltammogram obtained for 0.1 mM Pb solution at the PDE with a supporting electrolyte of 0.3 M acetic acid in the presence and absence of Cl<sup>-</sup> ions. In the absence of Cl<sup>-</sup> the resulting voltammograms exhibited one cathodic peak on the forward negative going scan and two anodic peaks on the return positive scan. The cathodic peak results from the deposition of Pb<sup>2+</sup> ions from solution to the electrode surface with the subsequent anodic peak resulting from the stripping of different layers of Pb metal film adsorbed at the electrode surface. These studies suggest the possibility of using these PDEs for the determination of Pb using anodic stripping voltammetry, the formation of such adsorbed layers is necessary for the accumulation step.

In previous studies at carbon electrodes the addition of Cl<sup>-</sup> ions to the supporting electrolyte has been shown to greatly improve the voltammetric behaviour of metal ions such as Pb [43-45]. Further cyclic voltammetric investigations showed that the addition of Cl<sup>-</sup> ions to the 0.3 M acetic acid supporting electrolyte solution resulted improved peak shapes and lower  $\Delta E_p$  values. Figure 2 shows the resulting improvement obtained by the addition of 0.25 M KCl. Consequently, further studies were undertaken using supporting electrolyte solution of 0.3 M acetic acid 0.25 M KCl.

### Effect of Accumulation Potential

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3 Linear sweep voltammetry was used to investigate the effect of applied potential was studied for a 0.1  
4 mM  $\text{Pb}^{2+}$  solution over the range  $-0.55$  V to  $-1.3$  V (vs. SCE) using an accumulation time of 15 s in  
5 still solution. Under these conditions, the magnitude of the stripping peak was found to increase with  
6 increasing negative potential, until forming a plateau between  $-1.0$  V and  $-1.3$  V (vs. SCE) (Figure  
7 3). Consequently, further investigations were made using an applied potential of  $-1.1$  V (vs. SCE).  
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#### 10 11 12 13 14 **Effect of Voltammetric Waveform**

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16 In previous investigations we have shown the improved analytical performance that can be gained by  
17 using the differential pulse waveform compared to linear sweep voltammetry [46]. Figure 4a shows a  
18 typical LSV obtained for 415 ng/mL Pb using an accumulation time of 120 s. This resulted in poor  
19 analytical performance, with a small peak at  $-0.56$  V on a sloping baseline recorded. However, using  
20 the same accumulation potential and time, three well-defined stripping peaks for Pb were obtained by  
21 differential pulse voltammetry (Figure 4b). The small voltammetric responses seen in the absence of  
22 Pb are believed to result from the heterogeneity of the electrode surface. Consequently, further  
23 investigations were made using this waveform.  
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#### 33 34 **Effect of Accumulation Time**

35 As it was intended to use these PDEs for the determination of low concentrations of  $\text{Pb}^{2+}$ , further  
36 studies were undertaken to ascertain the effect of accumulation time using an applied potential of  $-1.1$   
37 V (vs. SCE) for a 415 ng/mL  $\text{Pb}^{2+}$  solution in the optimised electrolyte. Figure 5 shows the resulting  
38 effect of accumulation time on the peak current ( $i_p$ ). Peak currents for all three (i, ii and iii) anodic Pb  
39 stripping peaks were found to increase with time. Peak current of peak (i) was found to be the most  
40 sensitive, and a linear relationship with time was found up to 240 s. Beyond this time  $i_p$  continued to  
41 grow but exhibited a quasi-linear relationship. Both the anodic peaks (ii) and (iii) showed a similar  
42 behaviour, but were found to be less sensitive and as a result further analytical investigations were  
43 made using peak (i).  
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53 The formation of multiple stripping peaks has been previously reported at solid electrodes [37,46,47].  
54 The extra peaks (ii and iii) with more positive peak potential ( $E_p$ ) values than the *main peak* (i) are  
55 believed to result from stripping of the first monolayer of Pb bound to the electrode surface with the  
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3 greatest energy compared to the bonding of subsequent layers. The greater bounding energy  
4 consequently requires greater energy, resulting in increased positive potentials required for their  
5 stripping. The heterogeneous nature of the electrode surface results in the appearance of more than  
6 one of these extra peaks results from the bounding energy of this monolayer being different from site-  
7 to-site on the electrode surface.  
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### 14 **Calibration Studies by Differential Pulse Anodic Stripping Voltammetry**

15 A calibration study was performed on standard  $\text{Pb}^{2+}$  solutions over the range 83 ng/mL and 915  
16 ng/mL using a deposition potential of -1.1 V and deposition time of a 200 s (Figure 6). It was found  
17 that two different calibration ranges were obtained over the range studied. The slope between 83 and  
18 330 ng/mL was 1.06 nA/ng/mL and between 330 and 915 ng/mL was 1.80 nA/ng/mL. This behaviour  
19 may be explained by a change in the way the multilayer of Pb is deposited above some critical  
20 thickness [37,46,47]. Such behaviour has been reported at graphite electrodes and is indicative of the  
21 deposition of metals, such as Pb on carbon substrates [37,46].  
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### 31 **Analytical Application**

32 The PDEs were evaluated by carrying out Pb determinations on drainage water obtained from  
33 University of the West of England, UK. A 5 mL aliquot of the sample was diluted with sufficient  
34 acetic acid and KCl solution to give a 10 mL 0.3 M acetic acid/0.25 M KCl. The deposition time and  
35 potential, as well as DPASV parameters were the same as used previously. The concentration of Pb  
36 was determined using the method of multiple standard additions and Figure 7 shows the effect of  
37 added standards to a typical drainage water sample. Table 2 shows the precision and recovery data  
38 obtained for the drainage water sample. These data demonstrate that the proposed method has  
39 promise for the determination of Pb in such water samples.  
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### 50 **Conclusion**

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52 This proof of concept study has shown pencil drawn electrodes to be low-cost, simple and rapid to  
53 fabricate and green. The redox behaviour of Pb at pencil drawn electrodes was investigated. Well-  
54 defined cathodic and anodic peaks could be obtained utilising an electrolyte comprising of 0.30 M  
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3 acetic acid, 0.25 M KCl. By using a deposition potential of  $-1.1$  V it was demonstrated that these  
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5 electrodes could be used in conjunction with DPASV for the trace determination of Pb with only  
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7 simple dilution of the sample with supporting electrolyte.  
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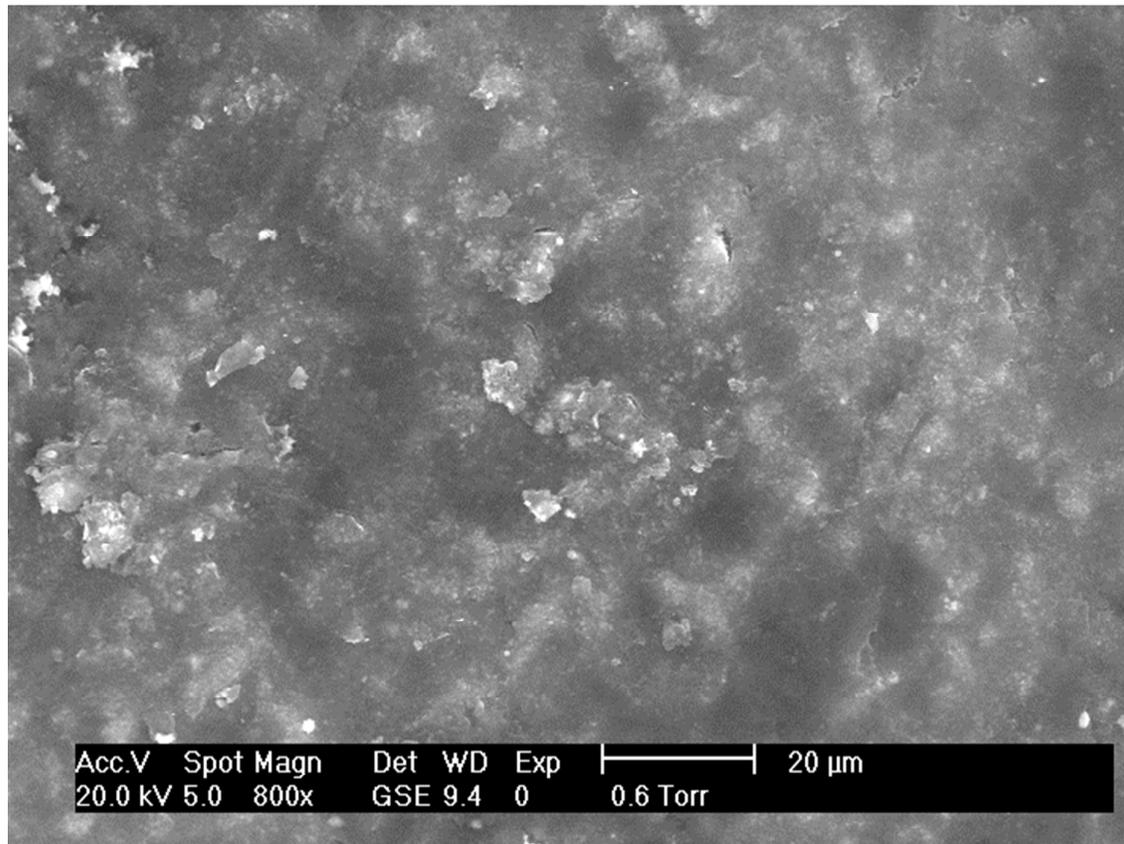
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10 The PDEs could be successfully used for the DPASV determination of low Pb concentrations  
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12 comparable to those reported in a number of environmental water samples [48,49] without the need  
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14 for further modification. The present study utilised a deposition time of only 200 s. Consequently, it  
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16 should be possible to enhance the sensitivity of the assay significantly by extending this parameter. It  
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18 should then be possible to obtain detection limits similar to those obtained at other conventional  
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20 electrode materials [50,51].  
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23 It is envisaged that further work will be performed to develop these PDEs for trace detection of other  
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25 metal pollutants. Demonstrable improvements in selectivity have been reported using either the *in*  
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27 *situ* or *ex situ* deposition of metal thins of Bi [50], Hg [51] or Sb [52]. Consequently, it is believed  
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29 that a similar approach could be employed with these devices.  
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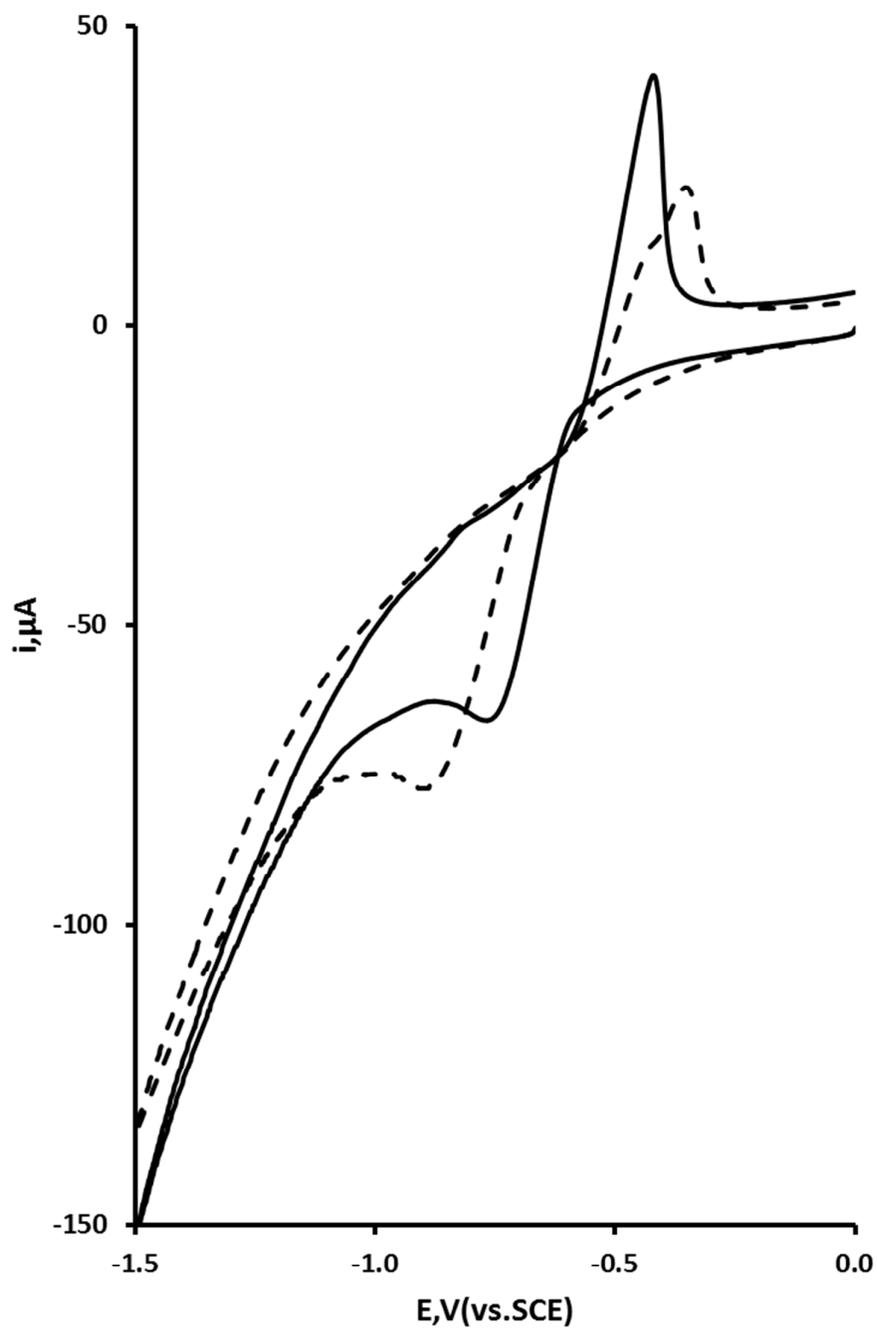
### 31 **Acknowledgements**

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33 I am grateful to the University of the West of England. David Patton is thanked for his assistance  
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35 with the SEM analysis.  
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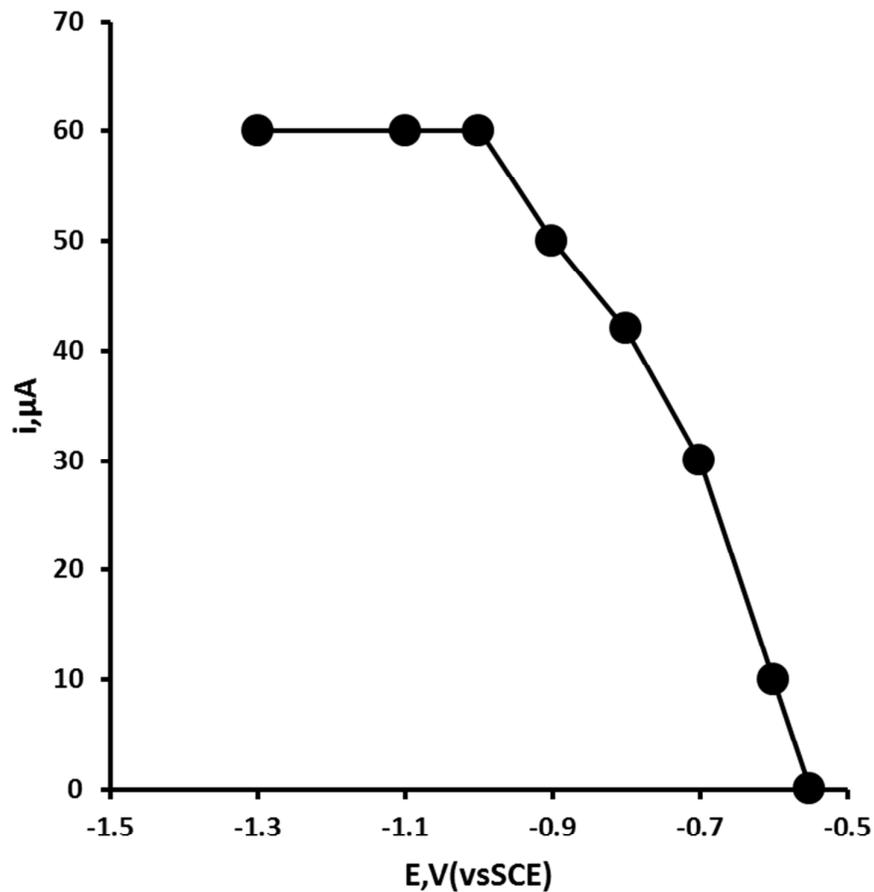
## Figures and Tables



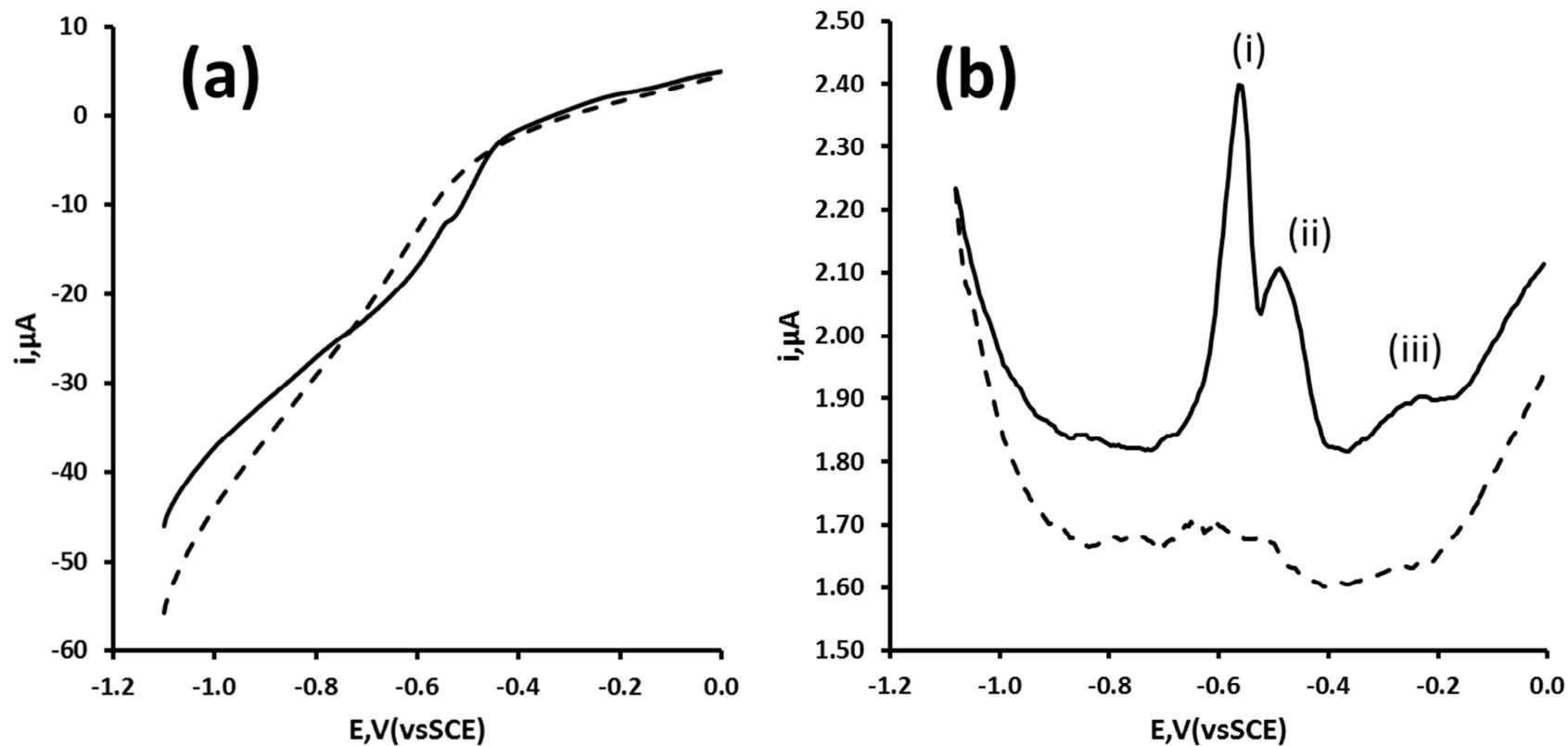
**Figure 1.** SEM image of a 6B pencil drawn electrode on PVC substrate.



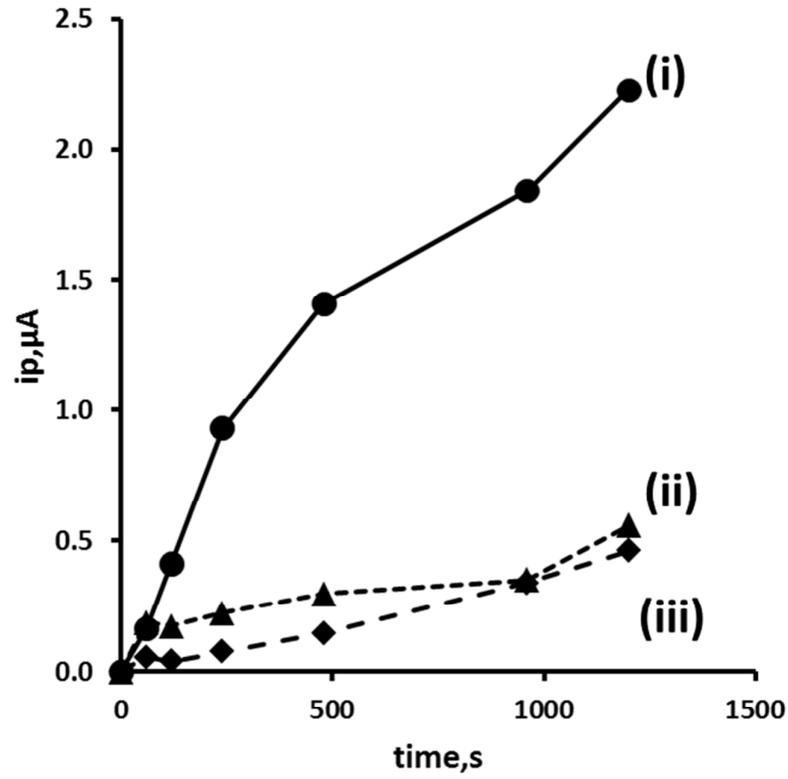
**Figure 2.** Cyclic voltammetric behaviour of 0.1 mM Pb at a drawn pencil in a 0.3 M acetic acid solution in the presence (solid line) of 0.25 M Cl and in the absence of Cl (dashed line). Voltammetric conditions: starting and end potential 0.0 V; switching potential -1.5 V; scan rate 50 mV/s.



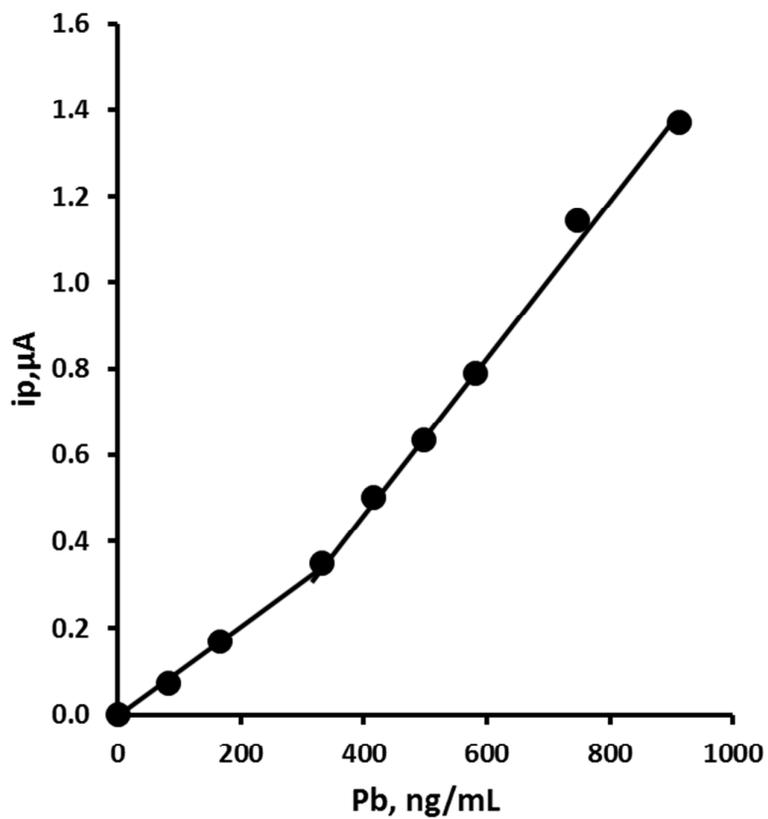
**Figure 3.** Effect of accumulation potential for a 0.1 mM  $\text{Pb}^{2+}$  solution in 0.3 M acetic acid containing 0.25 M KCl. Voltammetric conditions: Linear sweep stripping voltammetry, scan rate 50 mV/s; end potential 0.0 V.



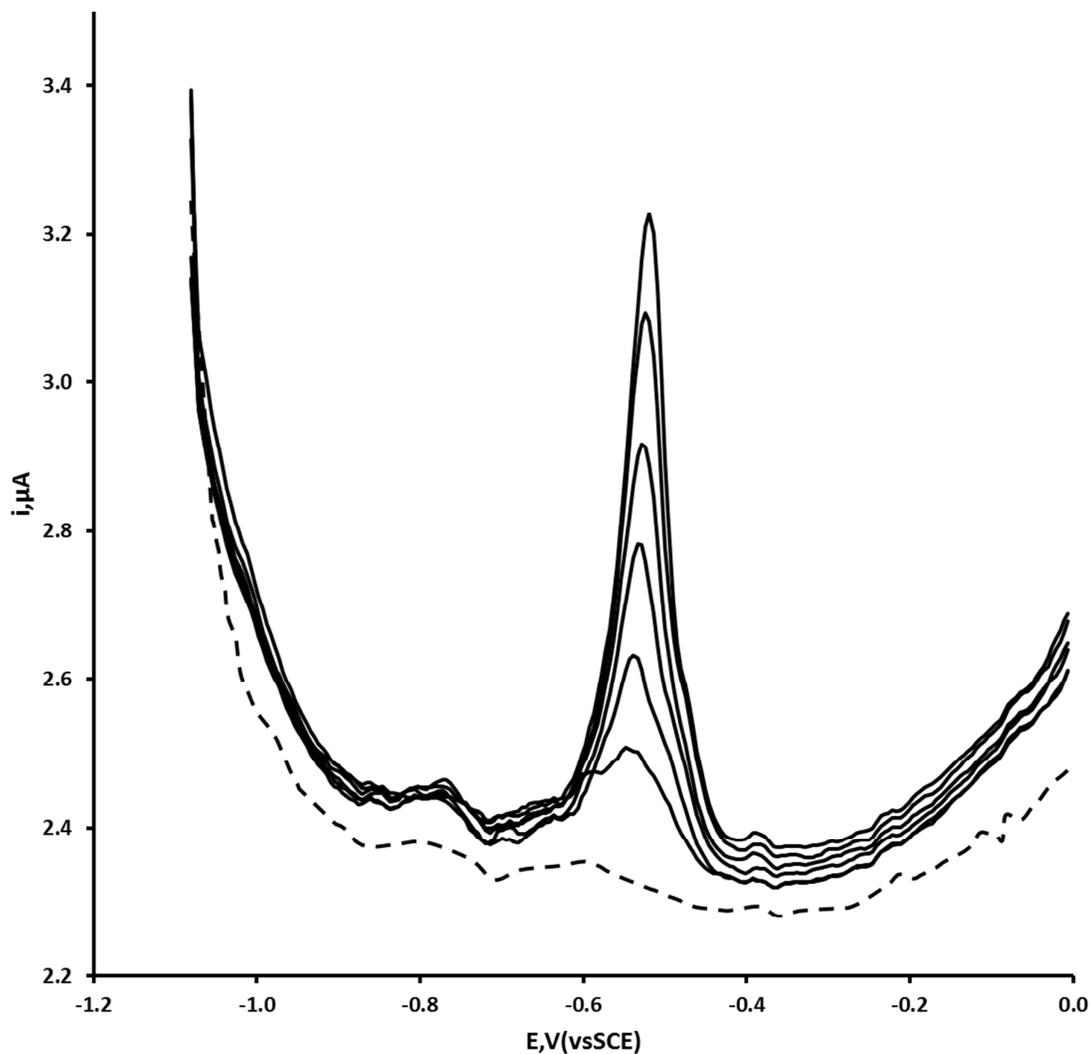
**Figure 4.** Effect of voltammetric waveform on the stripping voltammetric behaviour Pb. Solid line, in the presence of 415 ng/mL Pb and dashed line in the absence of Pb. (a) linear sweep (b) differential pulse voltammetry.



**Figure 5.** Effect of deposition time on the magnitude of stripping peak current for Pb. Deposition potential and other conditions as Figure 3.



**Figure 6.** Calibration plot for Pb obtained by DPASV; supporting electrolyte 0.30 M acetic acid, 0.25 M KCl.



**Figure 7.** DPASVs of a representative drainage water sample spiked with 166 ng/mL Pb with added concentrations of Pb: 0 ng/mL; 83.0 ng/mL; 116 ng/mL; 249 ng/mL; 332 ng/mL; 415 ng/mL Pb added. Dashed line representative DPASV of unfortified drainage water sample. Accumulation time: 200 s, deposition potential: -1.1 V (vs. SCE).

	Original Concentration [ng/mL]	Added [ng/mL]	Found [ng/mL]	% Recovery
1	nd	166.1	168.0	101.1
2	nd	166.1	166.0	99.9
3	nd	166.1	155.3	93.5
4	nd	166.1	182.3	109.7
5	nd	166.1	166.0	99.9
			mean	100.9
			sd	5.8
			%CV	5.7

**Table 2.** Recovery and precision data for Pb obtained on drainage water samples, nd = not detected.

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This paper describes the development and characterisation of an unmodified hand drawn pencil electrode for the differential pulse anodic stripping voltammetric determination of lead in an environmental water sample.

