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1 **Investigation into the voltammetric behaviour and detection of Selenium(IV) at**
2 **metal electrodes in diverse electrolyte media**

3
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13
14 **Abstract**

15 The voltammetric behaviour of selenium(IV) was studied at platinum and gold electrodes in sulphuric acid,
16 perchloric acid and potassium chloride media as a basis for its voltammetric detection. The best
17 voltammetric behaviour was recorded at gold electrodes with perchloric acid as the supporting electrolyte.
18 The concomitant presence of metals, such as copper or lead, and of model biomolecules, such as bovine
19 serum albumin, in the solution resulted in a deterioration of the electrochemical response for selenium(IV).
20 Quantitative detection of selenium(IV) by square wave anodic stripping voltammetry at both a millimetre-
21 sized gold disc electrode and a microband electrode array revealed linear responses to selenium
22 concentration in the ranges 5 – 15 μM and 0.1 – 10 μM , respectively, with 60 s preconcentration. The
23 sensitivities were 6.4 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ and 100 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$ at the disc and the microband array, respectively.
24 The detection limit at the microband electrode array was 25 nM, illustrating the potentiality of such
25 microelectrodes for the development of mercury-free analytical methods for the trace detection of
26 selenium(IV).

27
28 **Keywords:** Selenium, gold electrode, microelectrode array, anodic stripping voltammetry.

30 **1. Introduction**

31 Selenium is an essential element in animal and human nutrition and in environmental systems [1-3], although
32 its essentiality for plants remains controversial [4]. In biology, selenium is found in several forms including
33 selenoproteins (incorporating the modified amino acids selenocysteine or selenomethionine). The roles of
34 selenium in biological systems include cell defence against oxidative damage and viral infections, anti-
35 carcinogenic activity and control of thyroid hormone metabolism [5]. In the environment, selenium exists in
36 several oxidation states (+VI, +IV, 0, -II) [6] with Se(IV) the major species in aerobic and neutral-to-alkaline
37 environments and Se(VI) predominant in acidic environments [7]. Of the different oxidation states in which
38 Se can be found in nature, Se(IV) is by far the most toxic [6]; interestingly this is also the only electroactive
39 form of Se [8]. In biological systems Se is both an essential element and toxic, depending on concentration;
40 beneficial daily uptake for humans is in a very narrow range (50 - 220 $\mu\text{g day}^{-1}$) [2]. The maximum
41 allowable level of Se in drinking water is 10 $\mu\text{g L}^{-1}$ [9].

42

43 Several analytical methods have been proposed for the detection of trace levels of selenium, including
44 inductively coupled plasma mass spectroscopy [10], atomic absorption spectroscopy [11], neutron activation
45 analysis [12], inductively coupled plasma atomic emission spectroscopy [13] and the spectrophotometric or
46 spectrofluorimetric measurements of piaszelenol (reaction of Se(IV) with 2,3-diaminonaphthalene) [9,14-16].
47 All these approaches have the disadvantages of being time consuming, costly and not designed for in-the-
48 field applications. On the other hand, electrochemical methods, already proven to be very effective tools for
49 transition and heavy metal detection [17-20], are cost-effective, equally sensitive and suited to both
50 miniaturisation and in-the-field detection applications [21]. Consequently, reports on the use of stripping
51 voltammetric techniques for Se detection in diverse matrices such as food [22,23], atmospheric precipitates
52 [24], the marine environment [25,26] and natural waters [6,9,27,28] have appeared. Most of these employed
53 mercury-based electrodes [22-27], which hampers wide applicability of the proposed methods because of the
54 toxicity of mercury and the fact that it is banned for many applications including as an electrode material
55 [29]. Several alternative electrode materials have been investigated, including copper amalgam [6], bismuth
56 film [28], silver [30], gold [8,31], platinum [9,32] and ceramic composite [33]. The use of stripping
57 voltammetric techniques enabled very low limits of detection to be achieved, further improving the

58 capability of voltammetric techniques as analytical tools [34]. Both cathodic [33] and anodic [8] stripping
59 voltammetric techniques were used for selenium detection. Stozhko et al. [33] used ceramic composite
60 electrodes modified with 2,3-diaminophthalene to preconcentrate and detect Se(IV) in water with a detection
61 limit of $0.02 \mu\text{g L}^{-1}$ (ppb). Tan et al. [8] used square wave anodic stripping voltammetry (SWASV) at gold
62 microdisc electrode arrays for the detection of selenium in water samples, reporting a detection limit of 0.42
63 $\mu\text{g L}^{-1}$.

64

65 Improvements in electrochemical sensor performances have been shown to be achievable by sensor
66 miniaturisation (microelectrodes and their arrays) [33,35]. Microelectrodes are electrodes with at least one
67 dimension in the micrometre range or with at least one dimension smaller than the diffusion length of the
68 analyte [34,35]. The enhanced mass-transport rate achieved at microelectrodes leads to a faster response time
69 and greater sensitivity, although they have the disadvantage of very low currents. A solution to this is the use
70 of microelectrode arrays (MEAs), yielding a substantial improvement in the signal-to-noise ratio under
71 steady-state conditions [35].

72

73 The aim of the work reported herein was to investigate the electrochemical behaviour of Se(IV) in different
74 electrolyte media and at different electrode materials so as to provide the basis for the development of a
75 mercury-free voltammetric detection approach for this element. Studies of the interference of extraneous
76 metal ions and a model biomolecule were also performed. Finally, the detection of selenium at a MEA was
77 studied. The results presented provide the electrochemical basis for the analytical detection of Se(IV).

78

79 **2. Materials and methods**

80 *2.1 Reagents*

81 All chemicals were of analytical grade, were used without further purification and were sourced from Sigma-
82 Aldrich Ireland (Dublin, Ireland), unless otherwise mentioned. The Se(IV) stock solution was obtained from
83 Aldrich (UK) and the Cu, Ni and Zn 1000 mg L^{-1} standards were from BDH (UK). All solutions and
84 dilutions were prepared using ultra pure water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$) obtained from an Elga System
85 Maxima water purification unit (Elga Ltd., UK). All glassware was cleaned with concentrated HNO_3 and
86 rinsed thoroughly with ultrapure water prior to use in preparation of solutions. The Se(IV) stock solution was

87 stored at 4 °C as suggested in the literature [36] and the necessary dilutions were prepared freshly in plastic
88 containers prior to use.

89

90 2.2 Apparatus and electrode preparation

91 Electrochemical experiments were performed using a CHI620 electrochemical analyser with picoamp
92 booster & Faraday cage (CH Instruments, Texas, USA). The three-electrode electrochemical cell comprised
93 a platinum wire counter electrode, an Ag|AgCl|KCl(3 M) reference electrode (both CH Instruments, Texas,
94 USA) and one of the following working electrodes: a 2 mm diameter platinum disc electrode, a 2 mm
95 diameter gold disc electrode (both CH Instruments, Texas, USA) or a gold microband MEA. The MEA
96 consisted of three microband electrodes with widths of 20 µm, lengths of 500 µm and an inter-electrode
97 separation of 400 µm. The MEA preparation MEA was reported previously [35]. All the experiments were
98 performed in solution containing oxygen under ambient pressure. Prior to use, the working electrode surfaces
99 were cleaned as follows:

100 Gold and platinum disc electrodes: first, these were mechanically cleaned using a wet suspension of alumina
101 (in decreasing size, 1.0, 0.3, then 0.005 µm) and then rinsed and sonicated for 5 min in purified water. The
102 electrodes were then potential cycled in 0.1 M H₂SO₄ at 250 mV s⁻¹ until reproducible voltammograms were
103 obtained (*ca.* 75 cycles). The potential ranges were 0 – 1.6 V and –0.3 – -1.25 V for the gold and platinum
104 electrodes, respectively.

105 MEAs: first, they were treated with an oxygen plasma (March Plasmod) for 10 min at 100 W to remove
106 residual organic matter. They were then cycled 20-times in 0.1 M H₂SO₄ at a scan rate of 100 mV s⁻¹ in the
107 potential range 0 – 1.6 V.

108

109 2.3 Electrochemical measurements

110 The evaluation of the electrochemical behaviour of selenium at the different electrodes and in the different
111 media was performed by cyclic voltammetry (CV). CVs were performed by first scanning in the negative
112 direction and then switching the scan in the opposite direction so as to promote Se(IV) electrodeposition
113 followed by Se(0) stripping. The switching potential was varied in a systematic manner to gain an insight
114 into the deposition mechanism of selenium, *via* underpotential (UPD) and bulk deposition. The potential

115 ranges investigated were those within the analytically-useful range of the electrode materials; moreover the
116 lower limit of the CV was defined in order to avoid the formation of selenium hydride (H₂Se).

117

118 Linear sweep (LSASV) and square wave (SWASV) anodic stripping voltammetries were used in the
119 evaluation of the analytical performances of the different electrode configurations; in these evaluations the
120 UPD stripping process was used as analytical signal, due to its great analytical interest [8].

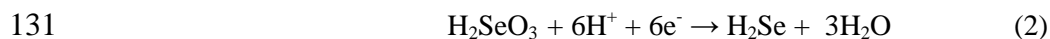
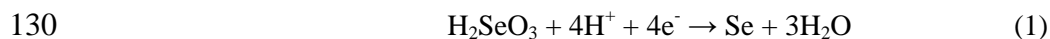
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122 LSASVs and CVs of Se(IV) were implemented at 10 mV s⁻¹. SWASV employed the following waveform
123 parameters: pulse amplitude 25 mV; step height 2 mV; frequency 20 Hz. The applied potentials used are
124 indicated in the text.

125

126 **3. Results and Discussion**

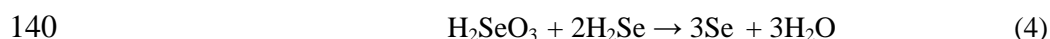
127 The electrochemistry of selenium at solid electrodes has been reported to be very complex. In acid medium,
128 the reduction of Se(IV), the only electroactive form of selenium, was proposed to follow two different
129 pathways, depending on the applied potential [32,37-39], (reactions 1 and 2).



132 Some authors proposed that reaction 2 is the result of reaction 1 followed by a further reduction of Se(0) via
133 reaction 3 [32].



135 When reduction is performed at higher potentials (typically between 0 and +400 mV, depending on the
136 reference electrode), Se(IV) reduction follows reaction 1 [37,39]; on the other hand when the potential is
137 swept to more negative values, reactions 2 and 3 can occur, resulting in the formation of H₂Se. Moreover
138 selenium hydride, in acid solution, is known to undergo a comproportionation reaction in the presence of
139 selenous acid (reaction 4) leading to the production of so-called red selenium [31,39].



141

142 *3.1 Evaluation of electrode materials and supporting electrolytes*

143 Two electrode materials (gold and platinum) and three electrolyte solutions were evaluated (0.1 M H₂SO₄,
144 0.1 M HClO₄ and 0.1 M KCl). These metals were selected for two reasons: (i) they have been reported to be
145 suitable materials for electrodeposition of Se [8,31,32,40] and (ii) they are routinely used in
146 photolithographic processes [34,35]. The most reported electrolyte solutions in the voltammetric detection of
147 selenium are 0.1 M H₂SO₄ and 0.1 M HClO₄ [8,31]. Here, the possibility of performing the electrochemical
148 detection of selenium in KCl was also studied, as this medium has a limited influence on metal speciation
149 and is representative of many water samples.

150 This evaluation was performed by recording CVs, according to the protocol described in section 2.3, at the
151 different electrode materials in the different electrolyte solutions containing 0.5 mM of Se(IV). Figure 1
152 shows CVs for gold (Figure 1A) and platinum (Figure 1B) disc electrodes in 0.1 M H₂SO₄ in the presence
153 and absence (insets) of 0.5 mM Se(IV). At the gold electrode (Figure 1A), a clear reduction peak was
154 recorded at *ca.* +300 mV. When the CV switching potential was +200 mV, a clear oxidation signal was
155 recorded at *ca.* +800 mV on the positive direction scan. As the switching potential was made more negative,
156 a second oxidation peak appeared at *ca.* +650 mV. Although this peak increased with a decrease in the
157 switching potential, those at +800 mV remained constant; this behaviour is typical of the underpotential
158 deposition and stripping of metals at solid electrodes. The maximum charge density for the peak at +800 mV
159 (i.e. the UPD stripping peak) was $4.02 \cdot 10^{-4} \text{ C cm}^{-2}$, corresponding to the stripping of *ca.* 1.1 nmol cm⁻² of Se
160 and consistent with the oxidation of a sub-monolayer of Se. Similar behaviour was reported by Perreira *et*
161 *al.*,[31]; the same authors also reported the presence of a third oxidation peak at a higher potential (*ca.* +1.1
162 V). This was attributed to the oxidation of a AuSe alloy resulting from the diffusion of bulk Se into the gold
163 [31].

164
165 At the platinum electrode (Figure 1B), selenium electrodeposition was characterised by a broad reduction
166 signal with a shoulder at *ca.* +200 mV. On reversing the potential, a single oxidation peak was recorded at
167 *ca.* +700 mV. As the CV switching potential was made more negative, the oxidation peak increased and
168 shifted to more positive potentials. The observed oxidation peak may be attributed to the oxidation of bulk
169 selenium, in analogy to that seen in HClO₄ [32]. However, the charge for this stripping process was only 4.4
170 $\cdot 10^{-4} \text{ C cm}^{-2}$ for the largest peak in Figure 1B, which is more consistent with stripping of a metal sub-
171 monolayer.

172

173 Although Santos *et al.* [32] reported that the stripping of the selenium UPD occurred in the same potential
174 region as platinum oxide formation, i.e. at higher potentials, it was in the HClO₄ electrolyte. However, the
175 formation of platinum oxide occurs at similar potentials in H₂SO₄ and HClO₄, so it may be assumed also that
176 the stripping of the selenium underpotential deposit occurs at a similar potential to the platinum oxide
177 formation and thus was not detected in this work. This would, of course, interfere with accurate measurement
178 of the UPD stripping process on platinum.

179

180 Figure 2 shows the CVs for Se(IV) in 0.1 M HClO₄ at the gold (Figure 2A) and platinum (Figure 2B)
181 electrodes. Perchloric acid was used previously as a supporting electrolyte for studies of the electrochemical
182 behaviour of selenium at solid electrodes [8,31,32,37]. The behaviour recorded at the gold electrode in this
183 medium (Figure 2A) was similar to that in H₂SO₄ (Figure 1A) in terms of deposition and stripping potentials.
184 These results were consistent with those reported by Alanyalioglu *et al.* [37] in a study of the
185 electrodeposition of selenium onto Au(111). Clear deposition and stripping of UPD and bulk Selenium were
186 presented [37] and the presence of two additional reductive waves at potentials more positive than the UPD
187 process were attributed to the reduction of physisorbed SeO₂ [37]. These reductive waves were not found in
188 the present study, probably due to the difference in the crystallinity of the gold surfaces used. Several authors
189 [8,31,32] also reported the presence of a further oxidation peak in the voltammogram at higher potentials on
190 thin film and sputtered gold electrodes, which was attributed to the oxidation of AuSe alloy.

191

192 In addition, similar behaviour was observed at a platinum electrode in HClO₄ (Figure 2B) to that in H₂SO₄
193 (Figure 1B). In both the cases a single stripping peak was recorded within the potential range investigated.
194 The potential of this peak is in agreement with that recorded by Santos *et al.* [32] for the oxidation of the
195 bulk deposited selenium. Notably, the electrochemical response in HClO₄ was lower than in H₂SO₄,
196 irrespective of the electrode material.

197

198 In 0.1 M KCl, the electrochemical behaviour of Se(IV) (Figure 3) was very different from that seen in H₂SO₄
199 and HClO₄. At both metal electrodes very similar behaviour was obtained: a reduction wave was evident at
200 *ca.* +100 mV with a corresponding oxidation peak occurring at *ca.* +575 mV (insets in Figure 3A and Figure

201 3B). As the CV switching potential became more negative, the height of the oxidation peak increased and its
202 potential shifted to higher potentials until a new, sharp reduction peak was recorded at *ca.* -375 mV (Figure
203 3A and Figure 3B). The appearance of this second reduction peak was associated with the progressive loss of
204 the oxidation peak. This new reduction process was associated with the formation of H₂Se (reaction 3); this
205 was corroborated by the fact that the peak occurred in the potential region where the reduction of Se(0) to
206 Se(-II) was previously reported [37,39] and by the progressive loss in Se stripping signal.

207

208 In acid solution and in the presence of high concentration of Se(IV), as suggested by Solaliendres *et al.* [39],
209 the generated H₂Se can undergo a comproportionation reaction (reaction 4) with the Se(IV) present to
210 generate further Se(0) on the electrode surface and in this way limit the loss of Se(0) from the electrode
211 surface. The progressive loss of the selenium oxidation signal seen here could be due to limiting of the
212 comproportionation reaction by the low concentration of H⁺ in this electrolyte, favouring the formation of the
213 hydride.

214

215 These evaluations clearly indicated that gold was the best substrate for selenium electrodeposition and
216 stripping voltammetric detection. Moreover, despite higher electrochemical responses recorded in H₂SO₄, the
217 HClO₄ electrolyte gave a better peak definition and better discrimination between the bulk
218 deposition/stripping and UPD.

219

220 3.2 Stripping voltammetry of selenium

221 Figure 4 shows the effect of the deposition time on the stripping response of selenium (0.15 mM) at a gold
222 electrode in 0.1 M HClO₄. Based on the previous experiments (Figure 2A), a deposition potential of -200
223 mV was chosen. For the shorter deposition times, a single stripping peak at *ca.* +900 mV was obtained. This
224 peak increased with the deposition time up to a maximum value (deposition time \leq 15 s). This behaviour
225 (Figure 4, inset) is typical of the stripping of a UPD layer from a solid electrode. For deposition times >15 s,
226 a second stripping peak appeared on the voltammogram at a lower potential (*ca.* +750 mV). This peak
227 increased linearly with deposition time (Figure 4, inset). Furthermore, for the longer deposition times, an
228 additional small peak was present (at *ca.* +1.1 V) in the region in which the oxidation of the AuSe alloy was
229 reported [31]. The appearance of this third peak also coincided with a decrease of the UPD peak, which is

230 consistent with the finding of Tan and Kounaves [8] that the UPD stripping peak was lost with long
231 deposition times, due to the formation of an Au-Se intermetallic compound.

232

233 To confirm that the peak at *ca.* +900 mV was related to the stripping of UPD selenium, the surface coverage
234 (Γ) was evaluated according to the equation[17]:

235

$$\Gamma = Q/(n.F.A)$$

236 where Q is the charge (C) under the voltammetric peak, n is the number of electrons exchanged in the
237 oxidation process, F is the Faraday constant (96485 C mol⁻¹) and A is the surface area of the electrode (cm²).

238 The value of n was taken to be 4 (according to reaction 1) and the geometric area of the electrode was used
239 (0.0314 cm²). This yielded a maximum selenium surface coverage of 1.6 ± 0.44 nmol cm⁻² following a 30 s

240 deposition period. This value was in agreement with the theoretical surface coverage for a monolayer of
241 UPD metal on a substrate (2 nmol cm⁻²) [17].

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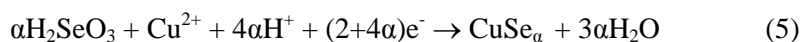
243 3.3 Interferences

244 In order to assess the possible practical utility of the gold electrode-based anodic stripping voltammetric
245 detection of selenium in biological or environmental samples, the influence of other metal ions such as
246 copper, lead, zinc and nickel and of a model biomolecule (bovine serum albumin, BSA) was investigated.

247

248 Copper and selenium are well known to interact during electrochemical reductions [6,38,41]. At mercury
249 electrodes, they form a bi-metallic compound Cu₂Se [6,38]. Piech *et al.*[6] took advantage of this property as
250 the basis for selenium detection. At solid electrodes, it has been reported that the presence of copper results
251 in an acceleration of selenium deposition with a relative improvement in selenium detection in adsorptive
252 stripping voltammetry [38]. It was also reported that the presence of a 100-fold excess of copper over
253 selenium interfered in detection of the latter by anodic stripping voltammetry at gold electrodes [42]. Marlot
254 *et al.* [43] proposed a mechanism for the formation of CuSe bimetallic compounds at gold electrodes
255 (reaction 5).

256



257 where α is a function of the relative concentrations of copper and selenium and of the electrolyte solution
258 used.

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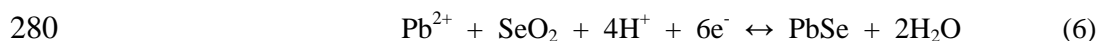
260 Figure 5A shows CVs of Se(IV) in the presence of increasing concentrations of Cu²⁺. When 5 μM of copper
261 was added to the 100 μM selenium solution, an additional reduction wave appeared at *ca.* +150 mV and with
262 an associated oxidation wave at +250 mV. Moreover the addition of copper resulted in a loss of the selenium
263 stripping response. Further increases of the copper concentration, up to 45 μM, did not result in any
264 substantial alteration in the selenium stripping peak in terms of shape or height. However, the UPD reduction
265 wave for selenium did become less well-defined, changing from a peak to a shoulder on the copper reduction
266 wave.

267

268 In Figure 5B, the voltammetric response of selenium before and after the addition of increasing
269 concentrations of lead in the range 50 – 350 μM, are shown. As can be seen, when 50 μM of Pb²⁺ was added
270 to the 100 μM Se(IV) solution, additional reduction oxidation peaks appeared at -100 mV and +100 mV, due
271 to the UPD and oxidation of lead, respectively. The presence of lead caused a broadening of the bulk
272 selenium oxidation peak. A loss in the selenium UPD reduction peak was also observed in the presence of
273 lead ions.

274

275 Lead and selenium are well known to form inter-metallic compounds (PbSe) [44]. Stretsov *et al.* proposed
276 two possible mechanisms for the formation of PbSe at a platinum electrode [44]. The first was *via* the
277 interaction of Se(-II) and Pb(II), while the second was *via* the reduction of both elements. Due to the fact that
278 the experimental conditions employed in the present work were not reducing enough to generate H₂Se, the
279 most probable route for PbSe formation is:



281 Figure 5C shows that upon addition of nickel, the only change was a loss of the selenium UPD stripping
282 peak after the first addition of nickel. In the case of zinc (Figure 5D), despite the fact that electrochemical
283 formation of ZnSe alloy has been reported in acid media [45,46], no interference was expected due to the
284 fact that ZnSe has been shown only to occur at elevated temperatures, with an optimum at 85 °C [45,46].

285

286 The effect of BSA, a model protein used in many electrochemical surface adsorption studies, on the
287 voltammetric response of Se(IV) was also investigated (Figure 5E). As expected [47], the adsorption of the

288 biomolecule on the surface of the electrode prevented the deposition/stripping of the selenium; this resulted
289 in a loss in intensity of the peak and in a shift to a more positive potential of the voltammetric stripping
290 signal .

291

292 3.4 SWASV: comparison of disc and microband array electrodes

293 Based on the results presented above, the analytical performances for the detection of selenium at gold
294 electrodes in 0.1 M HClO₄ were assessed in terms of the linear dynamic range, the sensitivity and the limit of
295 detection (LOD). SWASV was employed because of its ability to provide improved sensitivity. Here the
296 UPD stripping current was used exclusively as the analytical signal. Two types of gold electrodes were used,
297 a polycrystalline gold disc electrode and a gold microband electrode array (MEA). Figure 6 shows the
298 SWASVs for Se in the concentration range between 0.25 and 100 μM at the disc electrode (Figure 6A) and
299 at the MEA (Figure 6B); in both cases a deposition time of 60 s was employed. Clearly, the use of the MEA
300 resulted in an improvement in the sensitivity and the linear dynamic range, as seen by Tan and Kounaves on
301 their pioneering work on use of MEAs in selenium detection [8]. The linear dynamic ranges obtained were 5
302 – 15 μM for the disc electrode and 0.1 – 10 μM for the MEA. The sensitivities (slopes of the calibration
303 curves) of the electrode responses, expressed in current density units, were 6.4 μA μM⁻¹ cm⁻² and 100 μA
304 μM⁻¹ cm⁻², for the disc electrode and the MEA, respectively. This highlights the enhancement in sensitivity at
305 the MEA due to the enhanced diffusion rate. The LODs, based on three-times the standard deviation of the
306 blank response (3σ), were determined to be 1.2 μM (disk electrode) and 25 nM (MEA).

307

308 Figure 7 shows photographs of the MEA before (Figure 7A) and after (Figure 7B) performance of the
309 measurements used in construction of a calibration curve. Clearly, a dark deposit appeared on the MEA
310 surface following the electrochemical reactions. CV of this array in fresh 0.1 M H₂SO₄ indicated the
311 presence of both selenium and gold oxidation peaks (data not shown). This may be due to the formation of a
312 AuSe alloy, as reported by others [8,19,31] or by the fact that the stripping of the selenium from the gold
313 surface is not 100 % efficient, as suggested by Solaliendres *et al.* [39].

314

315 4. Conclusion

316 The electrochemical behaviour of Se(IV) at metal electrodes in a variety of electrolyte solutions was
317 examined. At gold electrodes in acid media (H₂SO₄ and HClO₄), Se(IV) exhibited two clear processes for
318 deposition of a monolayer (UPD) followed by the growth of a bulk layer. However, on platinum only a
319 single deposition peak (attributed to bulk deposition) was observed. The electrodeposition of Se(IV) in 0.1 M
320 KCl at gold and platinum electrodes was also investigated; it was found that the electrodeposition of
321 selenium occurred at both electrodes although this was not as clear as in the acidic media. Moreover, it was
322 shown that in this medium the reduction of selenium previously deposited on the electrode occurred to form
323 selenium hydride. These results confirmed the importance of the use of acid media for selenium detection.
324 Although the two acidic media provided similar behaviour, there was better resolution between UPD and
325 bulk deposition and stripping in the HClO₄ electrolyte. It was also found that gold was a more suitable
326 substrate than platinum for selenium electrodeposition and, as a result, for its electroanalysis. The presence of
327 copper or lead in the measurement solution was shown to result in a change of the voltammetric response to
328 selenium, resulting in interference; however, the addition of zinc or nickel did not influence the response to
329 selenium. The use of SWASV of selenium at an MEA was shown to provide better analytical performances
330 than at a disc electrode, showing a better linear dynamic range, sensitivity and LOD (25 nM). However, there
331 was both electrochemical and visual evidence for the formation of a AuSe alloy at the MEA, suggesting the
332 importance of single use electrodes in trace analysis of selenium. Overall, the information presented here
333 provides the basis for an electroanalytical method for detection of trace selenium(IV).

334

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338

339 **References:**

- 340 [1] S.E. Raptis, G. Kaiser, G. Tolg, *Fresenius Zeitschrift Fur Analytische Chemie*, 316 (1983)
341 105.
- 342 [2] M.P. Rayman, *Lancet*, 356 (2000) 233.
- 343 [3] J. Szpunar, *Analyst*, 130 (2005) 442.

- 344 [4] N. Terry, A.M. Zayed, M.P. de Souza, A.S. Tarun, *Annual Review of Plant Physiology and*
345 *Plant Molecular Biology*, 51 (2000) 401.
- 346 [5] W.X. Wang, J.Y. Li, H.M. Duan, J. Ha, S.F. Li, *Microchimica Acta*, 154 (2006) 143.
- 347 [6] R. Piech, W.W. Kubiak, *Electrochimica Acta*, 53 (2007) 584.
- 348 [7] B. Lange, C.M.G. van den Berg, *Analytica Chimica Acta*, 418 (2000) 33.
- 349 [8] S.H. Tan, S.P. Kounaves, *Electroanalysis*, 10 (1998) 364.
- 350 [9] F.A. Bertolino, A.A.J. Torriero, E. Salinas, R. Olsina, L.D. Martinez, J. Raba, *Analytica*
351 *Chimica Acta*, 572 (2006) 32.
- 352 [10] E.J. McCurdy, J.D. Lange, P.M. Haygarth, *Science of the Total Environment*, 135 (1993) 131.
- 353 [11] A. Larraya, M.G. Cobofernandez, M.A. Palacios, C. Camara, *Fresenius Journal of Analytical*
354 *Chemistry*, 350 (1994) 667.
- 355 [12] A.J. Blotcky, A. Ebrahim, E.P. Rack, *Analytical Chemistry*, 60 (1988) 2734.
- 356 [13] W.T. Buckley, J.J. Budac, D.V. Godfrey, K.M. Koenig, *Analytical Chemistry*, 64 (1992) 724.
- 357 [14] M.W. Brown, J.H. Watkinson, *Analytica Chimica Acta*, 89 (1977) 29.
- 358 [15] Y. Shimoishi, K. Toei, *Analytica Chimica Acta*, 100 (1978) 65.
- 359 [16] N.D. Michie, E.J. Dixon, N.G. Bunton, *Journal of the Association of Official Analytical*
360 *Chemists*, 61 (1978) 48.
- 361 [17] V. Beni, H.V. Newton, D.W.M. Arrigan, M. Hill, W.A. Lane, A. Mathewson, *Analytica*
362 *Chimica Acta*, 502 (2004) 195.
- 363 [18] Y. Bonfil, M. Brand, E. Kirowa-Eisner, *Analytica Chimica Acta*, 464 (2002) 99.
- 364 [19] G. Herzog, D.W.M. Arrigan, *Trac-Trends in Analytical Chemistry*, 24 (2005) 208.
- 365 [20] G. Herzog, V. Beni, P.H. Dillon, T. Barry, D.W.M. Arrigan, *Analytica Chimica Acta*, 511
366 (2004) 137.
- 367 [21] V. Beni, V.I. Ogurtsov, N.V. Bakunin, D.W.M. Arrigan, M. Hill, *Analytica Chimica Acta*,
368 552 (2005) 190.
- 369 [22] C. Locatelli, *Electroanalysis*, 16 (2004) 1478.

- 370 [23] M. Panigati, L. Falciola, P. Mussini, G. Beretta, R.M. Facino, *Food Chemistry*, 105 (2007)
371 1091.
- 372 [24] M. Zelic, *Electroanalysis*, 20 (2008) 782.
- 373 [25] C. Locatelli, G. Torsi, *Microchemical Journal*, 65 (2000) 293.
- 374 [26] R.D. Riso, M. Waeles, S. Garbarino, P. Le Corre, *Analytical and Bioanalytical Chemistry*,
375 379 (2004) 1113.
- 376 [27] M. Ashournia, A. Aliakbar, *Journal of Hazardous Materials*, 168 (2009) 542.
- 377 [28] J. Long, Y. Nagaosa, *Analytical Sciences*, 23 (2007) 1343.
- 378 [29] E. Gustafsson, *Water Air and Soil Pollution*, 80 (1995) 99.
- 379 [30] T. Ishiyama, T. Tanaka, *Analytical Chemistry*, 68 (1996) 3789.
- 380 [31] C.F. Pereira, F.B. Gonzaga, A.M. Guarita-Santos, J.R. SouzaDe, *Talanta*, 69 (2006) 877.
- 381 [32] M.C. Santos, S.A.S. Machado, *Journal of Electroanalytical Chemistry*, 567 (2004) 203.
- 382 [33] N.Y. Stozhko, E.I. Morosanova, L.I. Kolyadina, S.V. Fomina, *Journal of Analytical*
383 *Chemistry*, 61 (2006) 158.
- 384 [34] V. Beni, D.W.M. Arrigan, *Current Analytical Chemistry*, 4 (2008) 229.
- 385 [35] A. Berduque, Y.H. Lanyon, V. Beni, G. Herzog, Y.E. Watson, K. Rodgers, F. Stam, J.
386 Alderman, D.W.M. Arrigan, *Talanta*, 71 (2007) 1022.
- 387 [36] I. Heninger, M. PotinGautier, I. deGregori, H. Pinochet, *Fresenius Journal of Analytical*
388 *Chemistry*, 357 (1997) 600.
- 389 [37] M. Alanyalioglu, U. Demir, C. Shannon, *Journal of Electroanalytical Chemistry*, 561 (2004)
390 21.
- 391 [38] Z. Fijalek, A. Lozak, K. Sarna, *Electroanalysis*, 10 (1998) 846.
- 392 [39] M.O. Solaliendres, A. Manzoli, G.R. Salazar-Banda, K.I.B. Eguiluz, S.T. Tanimoto, S.A.S.
393 Machado, *Journal of Solid State Electrochemistry*, 12 (2008) 679.
- 394 [40] P. Zuman, G. Somer, *Talanta*, 51 (2000) 645.

- 395 [41] D. Simkunaite, E. Ivaskevici, A. Kalinichenko, A. Steponavicius, *Journal of Solid State*
396 *Electrochemistry*, 10 (2006) 447.
- 397 [42] S.G. Hazelton, D.T. Pierce, *Analytical Chemistry*, 79 (2007) 4558.
- 398 [43] A. Marlot, J. Vedel, *Journal of the Electrochemical Society*, 146 (1999) 177.
- 399 [44] E.A. Streltsov, N.P. Osipovich, L.S. Ivashkevich, A.S. Lyakhov, V.V. Sviridov,
400 *Electrochimica Acta*, 43 (1998) 869.
- 401 [45] M. Bouroushian, T. Kosanovic, Z. Loizos, N. Spyrellis, *Journal of Solid State*
402 *Electrochemistry*, 6 (2002) 272.
- 403 [46] M. Bouroushian, T. Kosanovic, N. Spyrellis, *Journal of Applied Electrochemistry*, 36 (2006)
404 821.
- 405 [47] G. Herzog, D.W.M. Arrigan, *Analytical Chemistry*, 75 (2003) 319.
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408 **Figure legends.**

409

410 Figure 1. CVs of 0.5 mM Se(IV) in 0.1 M H₂SO₄ at gold (A) and platinum (B) disc electrodes. The insets
411 show CVs in the absence of Se(IV). Scan rate: 10 mV s⁻¹.

412

413 Figure 2. CVs of 0.5 mM Se(IV) in 0.1 M HClO₄ at gold (A) and platinum (B) disc electrodes. The insets
414 show CVs in the absence of Se(IV). Scan rate: 10 mV s⁻¹.

415

416 Figure 3. CVs of 0.5 mM Se(IV) in 0.1 M KCl at gold (A) and platinum (B) disc electrodes. The insets show
417 expanded views of the region for stripping of selenium from the surface. Scan rate: 10 mV s⁻¹.

418

419 Figure 4. Linear stripping voltammetry of 0.15 mM Se(IV) in 0.1 M HClO₄ at a gold disc electrode.
420 Deposition times: 0, 5, 15, 30, 45, 60, 90, 120 and 180 s. Deposition potential: -200 mV. Scan rate: 10 mV s⁻¹.
421 Inset: peak current versus deposition time for the UPD (+ 900 mV) and bulk (+ 750 mV) stripping signals.

422

423 Figure 5. CV of 100 μM Se(IV) in 0.1 M HClO₄ at a gold disk electrode with increasing concentrations of
424 (A) Cu, (B) Pb, (C) Ni, (D) Zn and (E) LSV of 1 mM of Se(IV) in the presence of increasing concentrations
425 of BSA. Scan rate 10 mV s⁻¹.

426

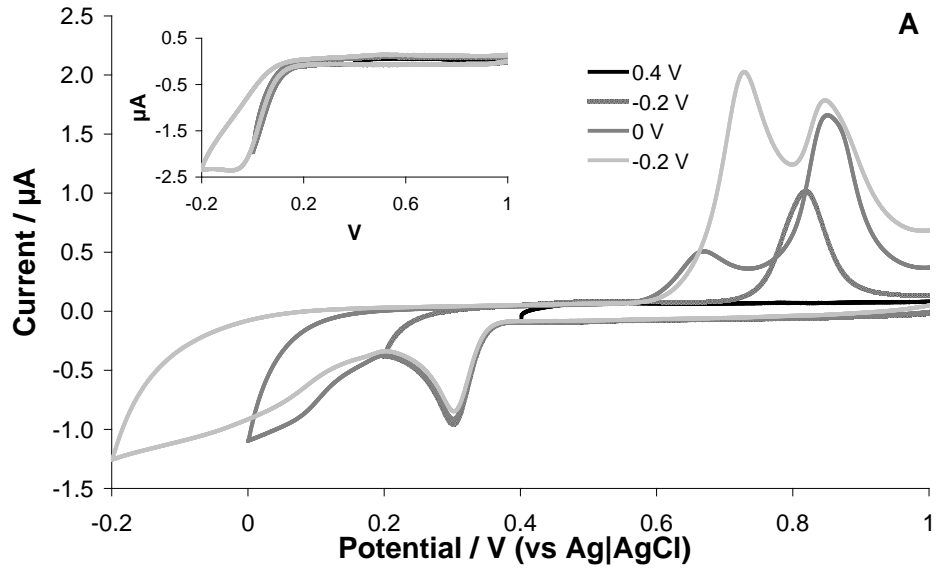
427 Figure 6. Square wave anodic stripping voltammetry of increasing concentrations of Se(IV) in 0.1 M HClO₄
428 at (A) a gold disk electrode and (B) a microband MEA. The concentrations of selenium investigated were:
429 0.25, 0.5, 1, 5, 10, 25, 50 and 100 μM. Deposition potential: 0 mV; deposition time: 60 s. Squarewave
430 parameters: pulse amplitude: 25 mV; step height: 2 mV; frequency: 20 Hz.

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432 Figure 7. Photographs of the MEA (A) before and (B) after running a series of SWASV experiments for
433 construction of a calibration curve.

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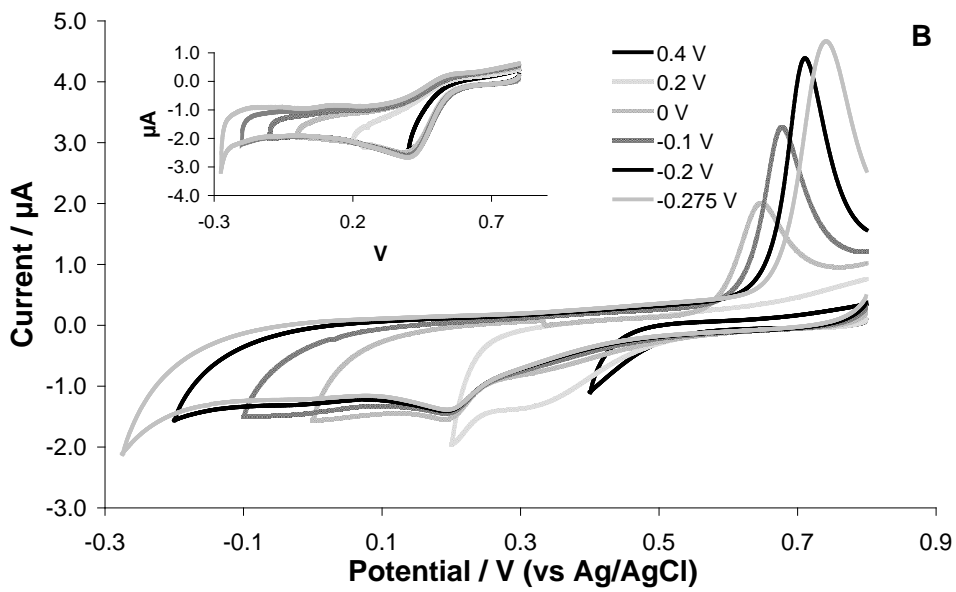
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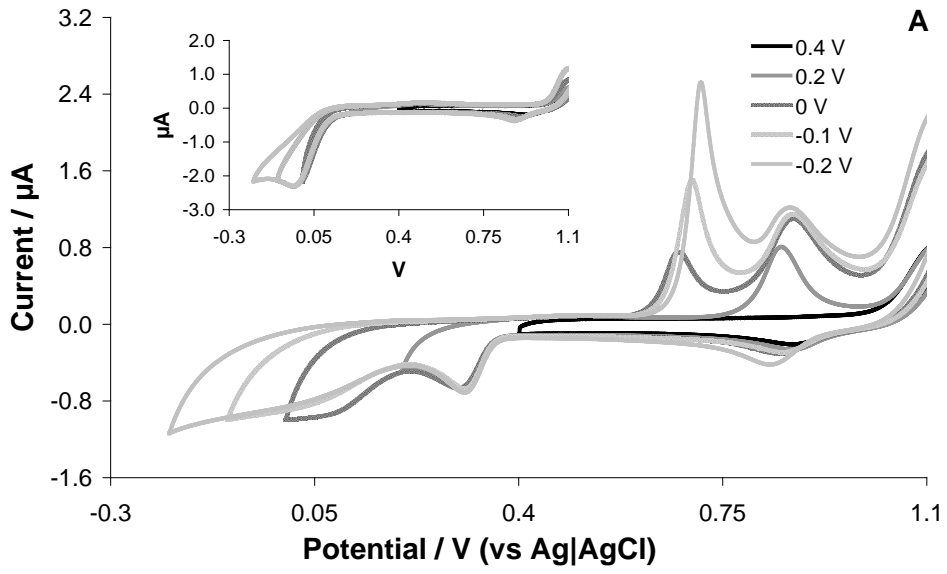
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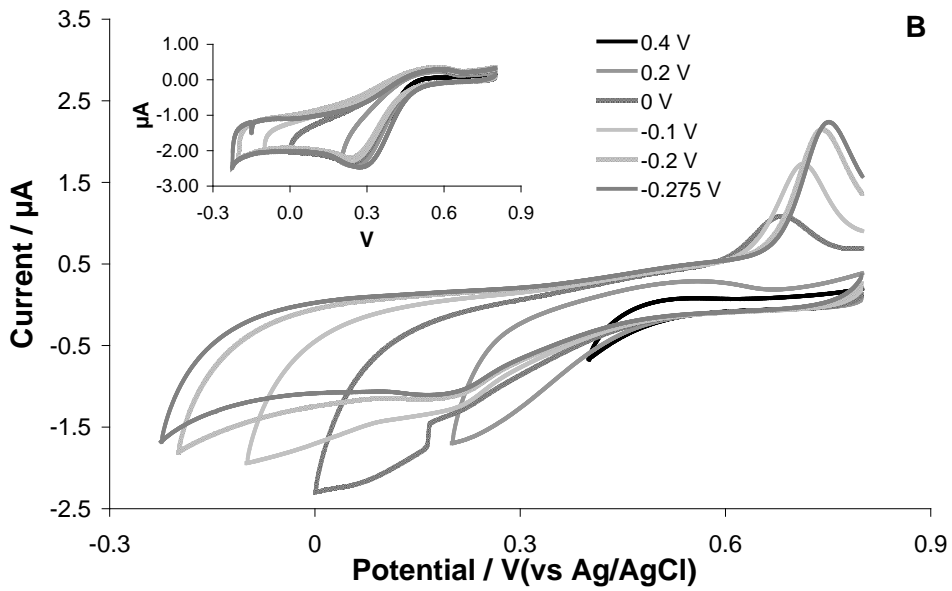
Figure 1

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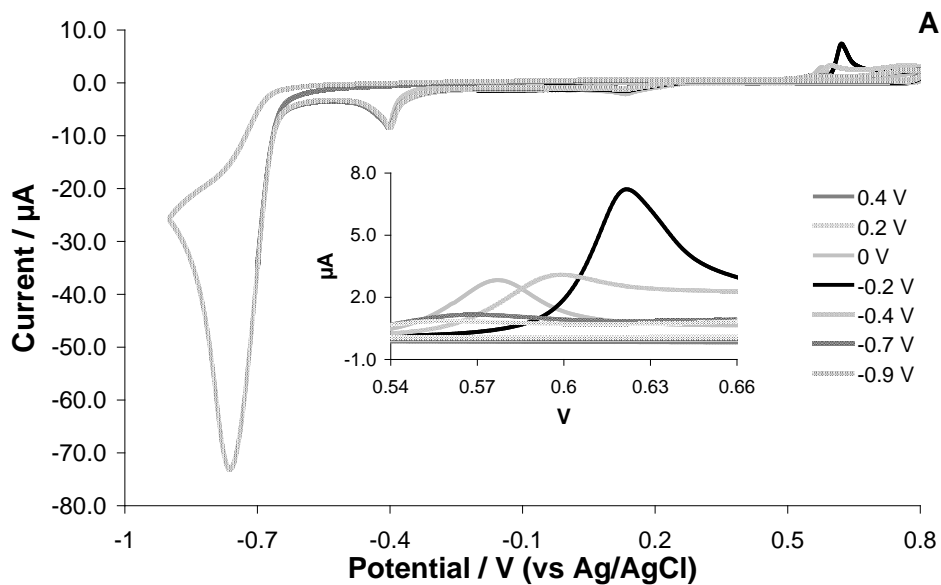
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Figure 2

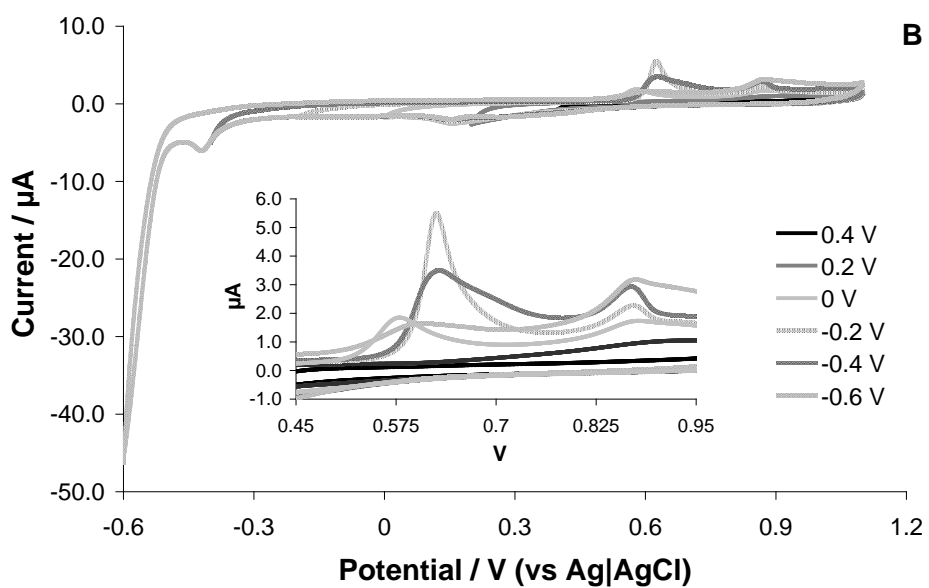
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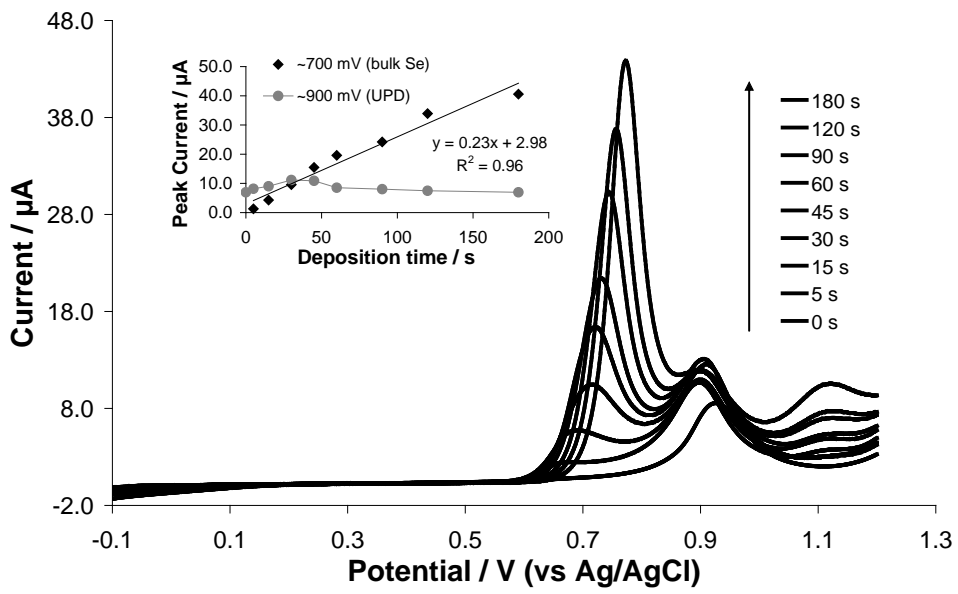
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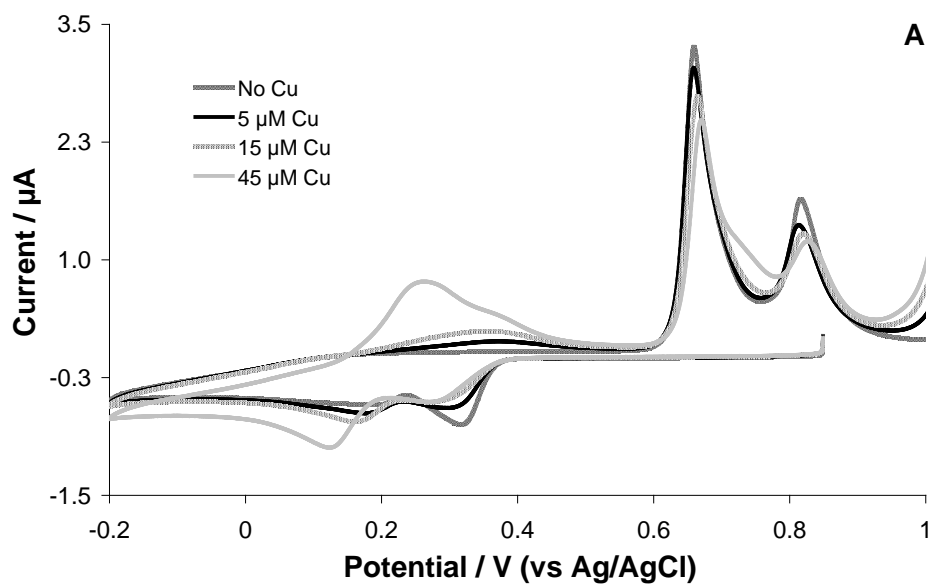
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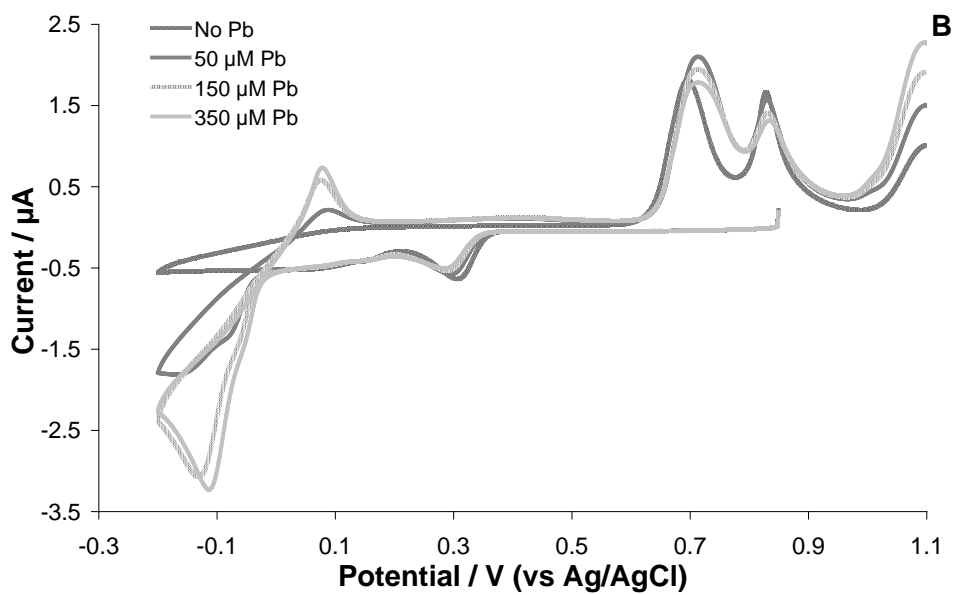


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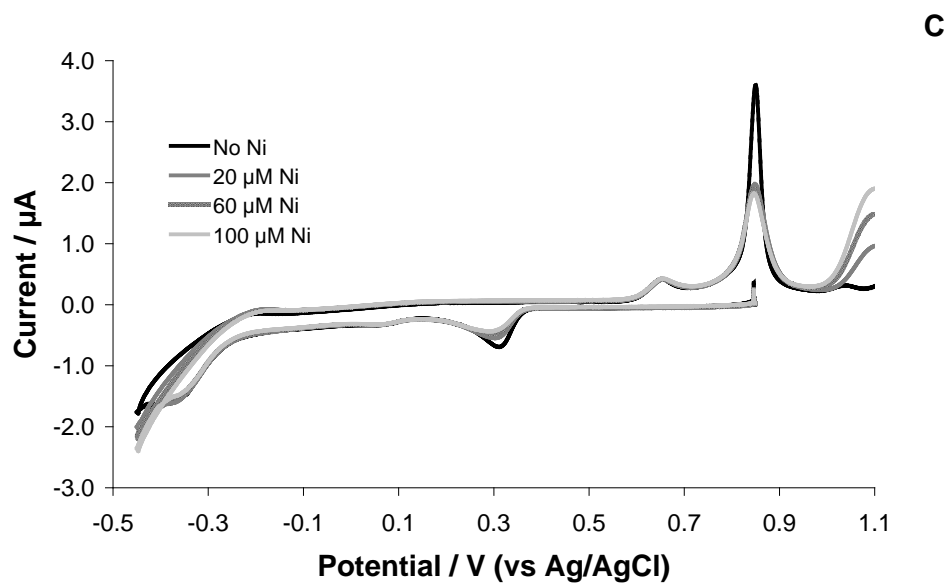
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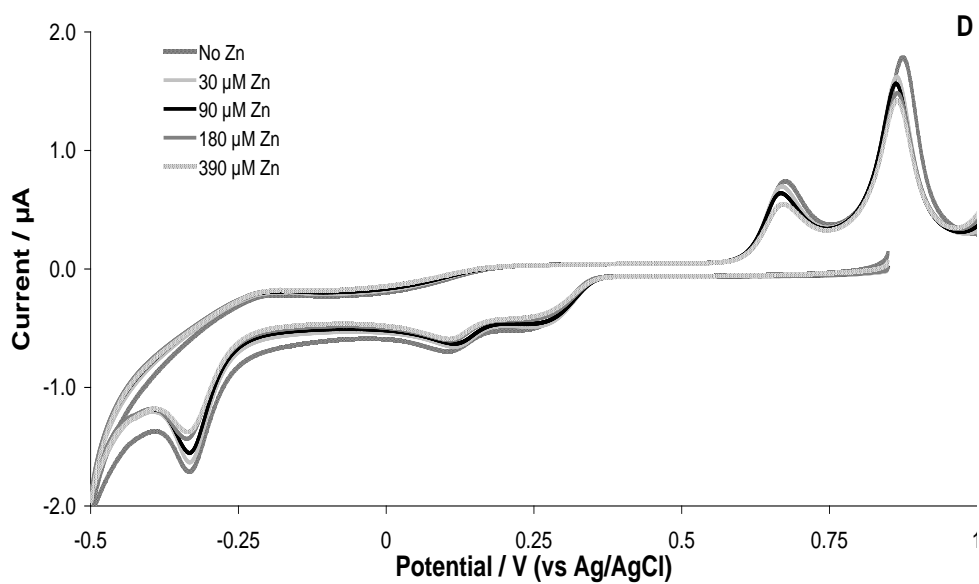
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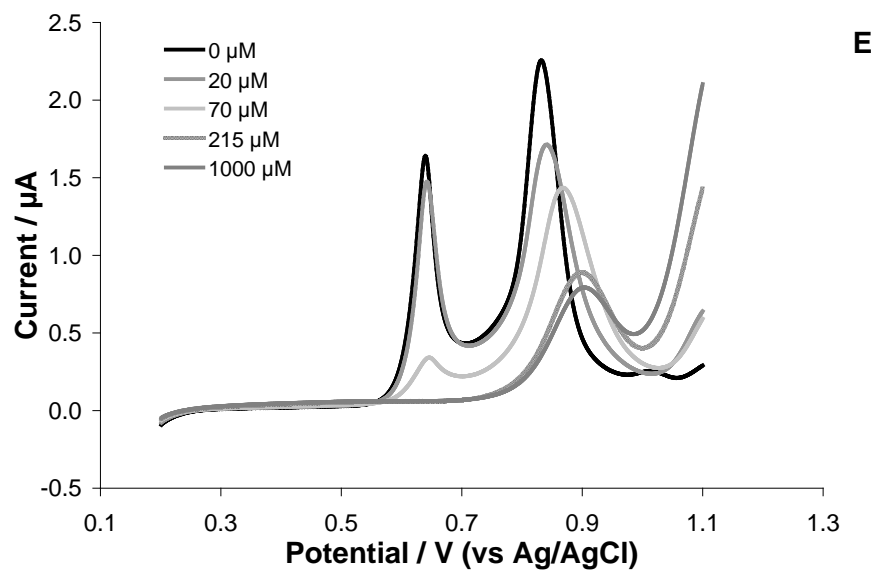
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Figure 5

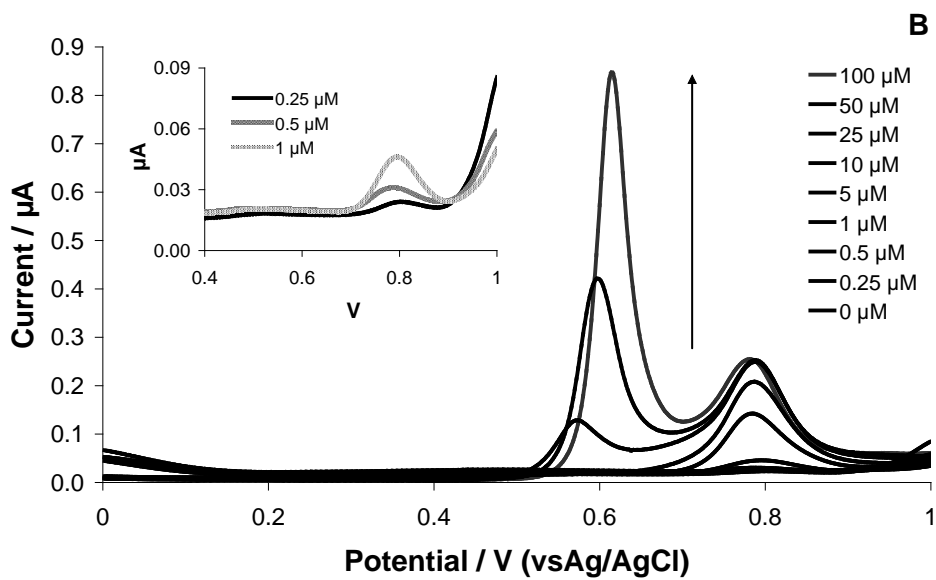
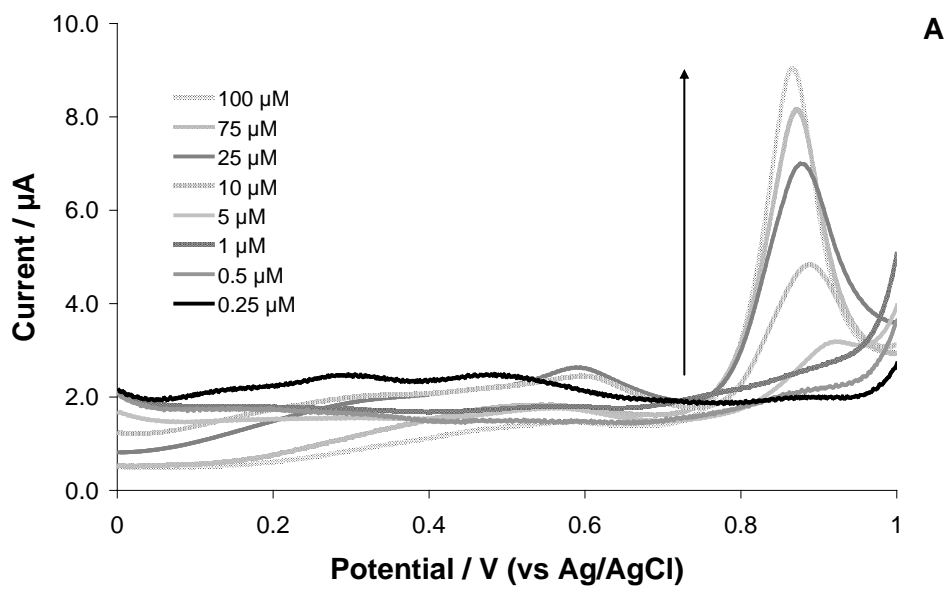


Figure 6

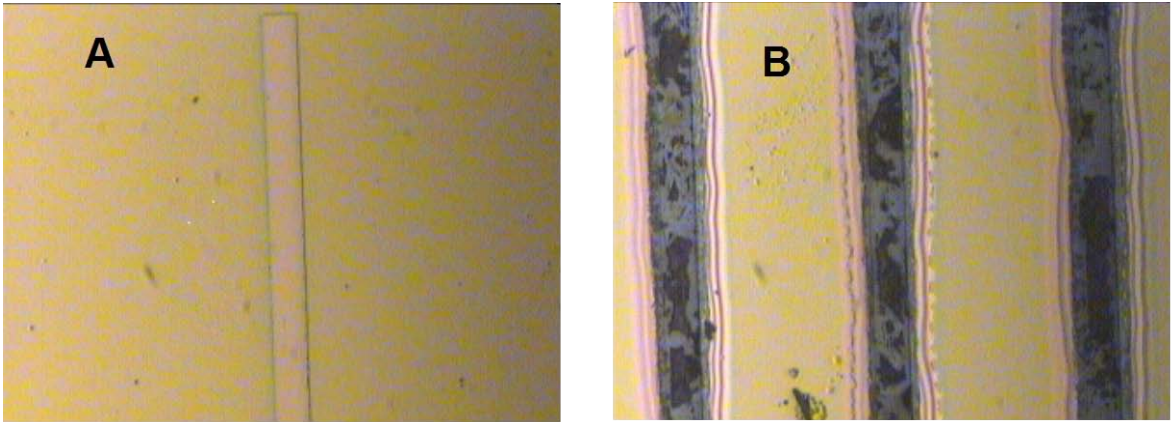


Figure 7