

## **Determination of iodide and total iodine in estuarine waters by cathodic stripping voltammetry using a vibrating silver amalgam microwire electrode**

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## **Abstract**

Iodide in natural waters is an important nutrient to aquatic organisms and its determination is of relevance to marine aquaculture. For this reason it is of interest to have a simple analytical method for determination of iodide in water samples. Iodide in seawater can be determined electrochemically by cathodic stripping voltammetry (CSV) with a mercury drop electrode which has environmental drawbacks. In an attempt to minimise the use of mercury in voltammetry, a vibrating silver amalgam microwire electrode is used here for the determination by CSV of iodide speciation in natural waters including seawater. Microwire electrodes were made from silver wires (diameter: 12.5  $\mu\text{m}$ ) and electrochemically coated with mercury. The electrode surface was stable for extended periods of analyses (at least one week) and was then replaced. The optimised conditions include a pH 8, a frequency of 500 Hz and a deposition time of 60 s, among others. The microwire was reactivated between scans using a conditioning potential at -3 V for 1 s. The detection limit for iodide in seawater was found to be 0.7 nM I<sup>-</sup> at a deposition time of 60 s. The response increased linearly with the concentration of iodide in seawater up to 100 nM I<sup>-</sup>. The method was successfully applied to various samples from the estuary of the river Mersey (Liverpool Bay). An existing procedure for iodine speciation was modified to enable determination of iodate and total iodine as well as iodide in estuarine waters.

## **Keywords**

Iodide; iodate; total iodine; Silver microwire electrode; Cathodic stripping voltammetry; Vibrating electrode.

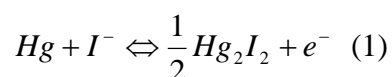
## Introduction

Iodine (I) is one of the biologically essential minor elements in seawater, and is essential in human nutrition [1,2]. In seawater it exists mainly as iodide ( $I^-$ ) and iodate ( $IO_3^-$ ) along with a small fraction of organic iodine compounds at a total concentration of about 450 nM at a salinity of 35 [3–6]. The distribution of iodide and iodate in seawater varies with water depth, geographical location, oxygen concentration and photochemical and biological mediation of the iodide/iodate equilibrium [7–10]. Iodide has marine importance as a nutrient for fish [11] and is potentially lost by oxidation to iodate during ozonation of the water in marine fish farms [12]. Seawater is a natural source of iodide but the major species of iodine is usually iodate [10], which is thermodynamically more stable in the presence of dissolved oxygen [13,14]. Iodate is the predominant species of dissolved iodine in ocean waters [9], however in surface waters and estuarine and coastal waters iodide may amount to a larger fraction [15–18]. It is thought that iodide is formed in surface waters in a concentration range between 50–250 nM as an unintended by-product by enzymatic reduction of iodate by organisms using nitrate reductase [19,20]. In anoxic seawater, e.g., the Black Sea, or in oxygen minimum zones in the open ocean, iodine is present almost entirely as iodide [15,21]. An organic fraction of iodine exists at several orders of magnitude smaller concentration than that of the inorganic species [22]. Determination of the speciation of iodine in seawater helps understanding the redox state of the marine environment.

Several methods exist for the determination of iodine in water samples [23], including capillary electrophoresis [24], ion chromatography [5,25,26], high-performance liquid chromatography [27], gas chromatography [28], spectrophotometry [29], spectrofluorimetry [30,31], amperometry and potentiometry [32,33], as well as voltammetry [14,34,35], among others. An advantage of voltammetry is that the iodine speciation can be determined at trace levels. The hanging mercury drop electrode (HMDE) has been successfully applied to

determine iodide in seawater with a limit of detection of ~0.1 nM [14,35,36]. Differences in the methods to detect iodide and iodate are related to the water pre-treatment and can involve polarographic detection of iodate. Both iodide and iodate are determined in a speciation method in which the iodide is detected by CSV using the HMDE after reduction of iodate to iodide to get total iodine with a detection limit for iodide and total iodine of 0.1 and 0.2 nM, respectively [35]. The response range was linear up to 400 nM of iodide.

The electrochemical determination of iodide is based on its interaction with mercurous ( $\text{Hg}_2^{2+}$ ) ions originating from the electrode surface [37]. The mercurous-iodide species is adsorbed (or precipitated) on the electrode surface according to equation 1, and the reduction peak is due to the reduction of the mercurous ions to  $\text{Hg}^0$  [36,38]:



The mercurous iodide is formed during the deposition step (forward reaction), and during the scan (which reverses the reaction) the iodide is returned to the solution and elemental mercury is formed. This means that the deposition step is also an electrochemical reaction in which current passes through the circuitry as the mercury is oxidised. This mercury oxidation was originally used for the polarographic determination of iodide using a dropping mercury electrode [38] and the opposite reaction has been used for the determination of iodide in seawater by cathodic stripping voltammetry (CSV) using a hanging mercury drop electrode (HMDE) in which the oxidised mercury species is deposited and subsequently reduced (and re-dissolved) again during the scan. [36]. A similar mechanism is valid for the reaction of chloride and bromide which both occur abundantly in seawater. The resulting mercurous halides have a very poor solubility ( $\log K_s(\text{Hg}_2^{2+})(\text{Cl}_2) = -16.8$  and  $\log K_s(\text{Hg}_2^{2+})(\text{I}_2) = -27.5$  [39]) and are therefore precipitated on the electrode surface during the deposition step. The peak for mercurous iodide is strongly shifted negative [37] as its solubility product is much smaller than that of chloride and bromide, and for that reason the iodide peak can be detected

in seawater in spite of much higher concentrations of the other halides. The voltammetric method (CSV) detects specifically iodide whereas iodate, which can be more abundant, is detected by CSV after its reduction to iodide [35]. The reduction to iodide is done chemically from weakly acidic condition (pH 2) using either sulphite [14] or ascorbic acid [35].

Advantages of a solid electrode are that it can be readily converted to flow analysis by fitting in a flow-cell, which is much easier than with the HMDE. A major advantage of the solid electrode is that the use of mercury is much reduced even though this electrode is mercury-coated. A vibrated microwire electrode is used here to improve the sensitivity. The electrode was electrochemically amalgamated with mercury prior to use. The surface was found to be stable and suitable for CSV without requiring re-coating for a week, and its very thin diffusion layer thickness leads to rapid analysis with sensitivity sufficient for environmental monitoring. Experimental parameters were optimised and the method was tested in water collected from the estuary of the river Mersey and Liverpool Bay.

## **Material and methods**

### *Apparatus*

Voltammetry was carried out using an Autolab voltammeter (Ecochemie, The Netherlands) connected to a VA663 electrode stand (Metrohm, Switzerland). The working electrode was a 12.5  $\mu\text{m}$  diameter silver microwire (Goodfellow Company, UK), the reference electrode was a double-junction Ag/AgCl, 3 M KCl, and an iridium wire of 0.15 mm diameter and 2 cm length was used as the counter electrode. The instrument was controlled by GPES 4.9 software.

### *Chemicals*

Reagents were of analytical reagent grade and solutions were prepared using Milli-Q deionised water (Millipore system, resistivity  $18 \text{ M}\Omega\text{cm}^{-1}$ ). Standard aqueous solutions of  $10^{-6}$  M iodide were prepared either weekly or at the beginning of a set of experiments from potassium iodide. Various pH buffer solutions were prepared depending on the range of studied pH: 1 M borate buffer (pH 9) from boric acid (Fisher Scientific, AnalaR grade, England) adjusted with 0.3 M NaOH (BDH, AristaR); 1 M borate buffer (pH 8) from boric acid (Fisher Scientific, AnalaR grade, England) adjusted with 0.3 M NaOH (BDH, AristaR); and 10 mM HEPES (pH 7) from N-2-hydroxyethylpiperazine-N'-2-ethane sulfonic acid (Sigma-Aldrich, Steinheim, Germany) adjusted with 0.3 M NaOH (BDH, AristaR). Hydrochloric acid was double-distilled. An aqueous solution containing 0.1 mM hydrazine was prepared from the hydrazine sulphate salt ( $\text{H}_4\text{N}_2 \cdot \text{H}_2\text{SO}_4$  Sigma-Aldrich, Steinheim, Germany). A solution containing 0.5 mM L-ascorbic acid,  $\text{C}_6\text{H}_8\text{O}_6$  (BDH, AnalaR grade, England) was used to reduce iodate quantitatively to iodide when necessary. The mercury plating solution containing 2 mM  $\text{Hg}^{2+}$  was prepared from monohydrated mercury nitrate (AnalaR grade, England) and acidified with 10 mM  $\text{HNO}_3$ .

#### *Microwire electrode preparation*

The silver microwire electrode was fabricated as before [40,41]. Briefly, the wire was heat-sealed in a 100  $\mu\text{L}$  plastic pipette tip and connected to the voltammeter via a lead that was press-fitted on the back-side of the tip. The tip was mounted on a vibrator unit allowing a vibration frequency of  $\sim 200$  Hz [42].

#### *Mercury plating*

Several scans were performed using cyclic voltammetry in a solution (25 mL) of 10 mM  $\text{HNO}_3$  between 0 to +0.4 V to check for normal electrode behaviour [43]. Subsequently,

mercury was added to a final concentration of 2 mM Hg. Mercury was electrochemically plated on the silver microwire at -0.4 V (10 min) from unstirred solution. The electrode was stored in Milli-Q deionised water. A plated electrode was typically used for about one week of experiments and was then replaced by a new one.

#### *General procedure to determine iodide*

In a glass voltammetric cell, 1 mL of seawater was diluted to 10 mL with Milli-Q water, and 100  $\mu$ L 1 M borate buffer was pipetted giving a final concentration of 10 mM borate (pH 8). The solution was deoxygenated by N<sub>2</sub>-purging for 5 minutes as the reduction peak for dissolved oxygen overlaps with that for iodide. The mercury-coated silver microwire electrode was activated at -3 V (1 s, with vibrator on) prior to each scan. Iodide was then accumulated at -0.1 V for 60 s (vibrator on). After a 1 s equilibration time (vibrator off) a voltammogram was recorded from -0.1 V to -1 V using the square-wave mode. The electrochemical parameters were as follows: 500 Hz frequency, 5 mV step potential and 25 mV amplitude. The electrochemical parameters are summarised in Table 1. The peak potential for iodide was -0.5 V (Fig. 1). Typically three scans were made and the peak-height averaged; the sensitivity was calibrated by internal standard additions to the same solution, by again recording the height (nA) of the peak for iodide. Iodide additions were chosen to be sufficient to at least double the initial iodide peak. The response for iodide was stabilised by addition of 0.1 mM hydrazine sulphate to the solution to prevent iodide oxidation.

#### *Sample collection and storage*

Seawater samples were collected at approximate high tide and covering a salinity range of between 19 and 32 in the Mersey Estuary in Liverpool Bay during a cruise with the Liverpool University research vessel Marisa in May 2013. Samples were collected using a plastic bucket

and filtered on-board through 1 and 0.2  $\mu\text{m}$  cellulose acetate filter cartridge (Sartobran 300, Sartorius), and subsequently stored dark and cold ( $\sim 5\text{ }^{\circ}\text{C}$ ) in 0.5 L HDPE bottles. Samples were diluted by a factor of 10 with Milli-Q water before the analysis to minimise interference by the major anions (chloride/bromide) and to ensure that the iodide concentrations fell within the dynamic range of the method.

## **Results and discussion**

Preliminary experiments using the silver amalgam electrode and voltammetric settings and procedures suitable for the HMDE [35] showed that the sensitivity for iodide in seawater was poor. As before [35], the sensitivity was much improved by dilution of the seawater to a lower salinity. It is likely that the major anions (chloride and bromide) form mercurous deposits similar to that of iodide [36] which interfere because they are present at much greater concentration than iodide, possibly saturating the electrode surface. Experiments using 10x, 5x and 2x diluted seawater were all found to give better sensitivity, with as drawback that the iodide concentration becomes diluted as well. Scans were relatively noisy in the undiluted seawater (salinity 35), whilst the sensitivity was greatest after 10-fold dilution to salinity  $\sim 3$ . The peak shifted positive by about 100 mV from -0.55 V in seawater to -0.45 V in the diluted seawater. The 10x dilution step was selected here for iodide detection. A seawater dilution factor of 5 is recommended when the HMDE is used [35]. Seawater contains up to  $\sim 500\text{ nM}$  combined iodide + iodate, which meant that the analytical range of interest for the 10x diluted water is 1-50 nM iodide.

The peak for iodide using the microwire electrode was located at -0.5 V, which is more negative than that (at -0.30 to -0.35 V) using the HMDE [35,36]. There was no need to add Triton-X-100 as recommended for the HMDE [36] as there was no obvious interference from



the major anions after dilution to a lower salinity, and as the peak was well removed from that for mercury oxidation.

Preliminary measurements of iodide in diluted SW showed a gradual decrease of the iodide peak (40% in 10 min) which was hypothesized to be caused by oxidation of  $I^-$  to  $I_2$  and  $I_3^-$  [44,45] or by reaction with mercurous ions from the electrode. The effect was minimised by addition of 0.1 mM hydrazine, a known reducing agent [46], suggesting that the decrease was a result of iodide oxidation, potentially catalysed by traces of elemental mercury. Addition of 0.5 mM ascorbic acid was used instead of hydrazine in later experiments as it was used also to determine the concentration of total iodide after reduction of iodate to iodide [35].

#### *Effect of pH*

The effect of varying the pH on the sensitivity for iodide was studied in seawater containing 50 nM  $I^-$ . Three different pH values were tested (7, 8 and 9) stabilised by pH buffers: HEPES 10 mM for pH 7 and borate buffer 10 mM for pH 8 and 9, using a square-wave frequency of 500 Hz and deposition time of 30 s. Highest sensitivity was obtained at pH 8, which is convenient as pH 8 is also the natural pH of seawater. The response was nearly the same at pH 9 (2% less) which means that any pH between 8 and 9 is suitable. The response was much (62%) lower at pH 7, which may indicate a possible reduction of iodide to other species such as  $I_2$  and  $I_3^-$  [44,45] at the lower pH.

#### *Effect of deposition potential*

The deposition potential was varied between -0.5 and 0 V in seawater containing 50 nM  $I^-$  (Fig. 2a): selection of the deposition potential is restricted at positive values by oxidation of the mercury film at potentials  $> 0$  V, whereas the mercurous-iodide is not deposited at potentials negative of the peak at -0.45 V. Best sensitivity was obtained at around -0.1 to -

0.05 V (Fig. 2a), which is similar to that found using the HMDE method [14,35]. The background current rises at potentials  $>-0.2$  V due to mercury oxidation associated with formation of the mercurous ion. At the same time the peak height for iodide increases greatly with deposition potentials increasing from  $-0.3$  to  $-0.1$  V (Fig. 2a). The background current is much greater at potentials  $>-0.1$  V, and the peak height for iodide decreased (Fig. 2a), which was ascribed to possible losses of the deposited mercury(I) layer due to formation of Hg(II). The decrease at more negative potentials is due to less formation of mercurous ions than at more positive potentials, and it may also be affected by the charge on the electrode: the zero point of charge in chloride solutions is near  $-0.5$  V [47,48], which means that at more positive potentials the electrode has a positive charge, attracting the negatively charged iodide ions. A deposition potential of  $-0.1$  V was selected for further experiments.

#### *Effect of varying the square-wave frequency*

The optimisation of frequency is important not only because of the speed of the analysis but also to minimise interference by dissolved oxygen: a broad peak due to the reduction of dissolved oxygen diffusing to the electrode is located  $\sim -0.2$  V; the height of the iodide peak is increased relative to that of oxygen at high scan rates (high frequency) as there is no contribution of diffusion to the iodide peak during the scan, which means that it may be possible to eliminate the oxygen interference. The effect of this parameter was investigated using 50 nM of iodide and a 30 s deposition time (Fig. 2b). The peak height increased linearly with the frequency until 500 Hz with a slope of unity, which is typical for the complete and electrochemically reversible reduction of an adsorbed species (see for instance [49] and [50]). At higher frequencies the signal became noisy due to a breakdown of the reversibility, combined with an increase of residual capacitance currents. Therefore, 500 Hz was chosen as the optimum value for further experiments.

### *Influence of varying the deposition time*

The deposition time was varied to determine when the electrode becomes saturated with iodide, and to find in what conditions best sensitivity is obtained. Different concentrations of iodide (10 nM and 100 nM I<sup>-</sup>) were compared. The peak height was found to increase initially linearly with the adsorption time, until levelling off at a response (100 nM I<sup>-</sup>) where apparently the electrode was saturated. It is likely that this saturation was not due to deposition of iodide alone but more likely in combination of other species of bromide and chloride (Fig. 2c), as the increase with deposition time diminished after about 60 s for both 10 and 100 nM iodide, but the response for 100 nM iodide was nevertheless much greater indicating that the electrode was not saturated with iodide. Generally best sensitivity was obtained using 60 s adsorption which was selected here for further optimisation.

### *Linear range and limit of detection*

The linear range and limit of detection for iodide was determined in diluted seawater, using a deposition time of 60 s. The rest of the electrochemical parameters were kept fixed (Table 1). In seawater, the response was found to increase linearly with the iodide concentration up to 100 nM, and non-linearly after that. The correlation coefficient was  $R^2 = 0.999$  and an equation of the linear regression  $y = 3.60 \pm 0.06 x + 5.42 \pm 3.02$  until 100 nM was obtained, where  $y$  and  $x$  were the peak current signal (nA) and I<sup>-</sup> concentration (nM), respectively (Fig. 2d). The standard deviation of the regression was found to be 4.78.

This dynamic range is slightly less than that of 130 nM using the HMDE [14]. The detection and quantitation limits for iodide were calculated from 3x and 10x the standard deviation of repeated scans for 3 nM iodide in seawater giving values of 0.7 and 2.5 nM I<sup>-</sup> respectively at a deposition time of 60 s. The DL is greater than that (0.1 nM) obtained using the HMDE [35].

Nevertheless the wire electrode is sufficiently sensitive to monitor iodide in coastal waters. The relative standard deviation of the peak height of repeated scans of 20 nM iodide was 5.3% (n = 7).

*Application to samples from the estuary of the Mersey and Liverpool Bay*

The method was applied to water samples collected from the estuary of the river Mersey and Liverpool Bay (England). Iodide was measured after sample dilution (10x) to final salinities between 1 and 3. Additionally, combined iodide and iodate was determined in two selected samples of different salinities. Total combined iodide was measured after reduction of all iodate to iodide using ascorbic acid after acidification (stations 1 and Liverpool Bay) to pH 2 using HCl [35]. The concentration of iodate is calculated from the difference between total and free iodide. Quantification was done by the standard addition method. The results (Table 2) showed a total concentration of I between 72 nM and 252 nM, and of combined iodide and iodate between 168 nM and 433 nM. The expected concentration of combined iodide in coastal water of a salinity of 35 is about 450 nM [4,18]. It is known that iodide concentration is stable in a large extent in seawater once it is formed by biological or abiological process [51]. Although probably small changes are possible in coastal waters it is not going to be a large difference. That is why the concentrations found in literature were considered as comparative values for our method. It was observed that the measured concentration of combined iodide (433 nM and 168 nM) in real samples with salinities of 32 and 19 respectively, were in accordance with the values found in literature [18] showing the relation between iodide and salinity.

The apparatus used here for the voltammetric detection of iodide was based in the laboratory. However, portable and battery powered potentiostats are available commercially. Combination of the vibrated silver amalgamated microwire electrode with a battery powered

potentiostat, and a small nitrogen tank for oxygen removal, would convert this to a potentially convenient field technique.

### **Conclusion**

This work demonstrates that an amalgamated silver microwire can be used to determine iodide and combined iodide and iodate in saline waters (estuarine or coastal origin). The microwire system is portable, and is therefore suitable for the field. The method has a higher limit of detection than the original methods based on the mercury drop electrode proposed by Wong and Zhang (1992) [14] and Campos et al. (1997) [35], but testing of the electrode on estuarine water samples showed that the wire electrode is sufficiently sensitive to monitor iodide in coastal waters.

### **Acknowledgements**

Financial support to Dr. Estrella Espada-Bellido from the University of Cadiz (Spain) for the promotion and support of research activity, and from the Ministry of Education, Culture and Sports for the mobility of academics and researchers overseas (José Castillejo) (Spain) is gratefully acknowledged.

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## Figure captions

Graphical Abstract. Reusable and portable vibrating silver amalgam microwire electrode for iodide detection in saline waters.

Fig. 1. CSV voltammogram of additions of iodide in seawater (Sal 3): 0, 2, 5, 10, 20 and 100 nM [I]. Experimental conditions: 10 mM borate buffer at pH 8, deposition potential -0.1 V, frequency 500 Hz, and 60 s as deposition time.

Fig. 2a. Effect of deposition potential on the stripping peak height of iodide in seawater (Sal 3) containing 50 nM I. Experimental conditions: 10 mM borate buffer at pH 8, frequency 500 Hz, and a 30s deposition time.

Fig. 2b. Influence of the voltammetric square-wave frequency on the stripping peak height of iodide in seawater (Sal 3) containing 50 nM I. Experimental conditions: 10 mM borate buffer at pH 8, deposition potential -0.1 V, and a 30s deposition time.

Fig. 2c. Influence of the deposition time on the stripping peak height of different concentrations of iodide in Sal 3 seawater (10 and 100 nM I). Experimental conditions: 10 mM borate buffer at pH 8, deposition potential -0.1 V, and square-wave frequency 500 Hz.

Fig. 2d. Response as a function of the concentration of iodide in seawater (Sal 3). Experimental conditions: 10 mM borate buffer at pH 8, deposition potential -0.1 V, frequency 500 Hz, and 60 s as deposition time.

Table 1. Electrochemical parameters for voltammetric analysis.

| Parameter              | Value  |
|------------------------|--------|
| Conditioning potential | - 3 V  |
| Duration               | 1 s    |
| Deposition potential   | -0.1 V |
| Deposition time        | 60 s   |
| Equilibration time     | 1 s    |
| Frequency              | 500 Hz |
| Step potential         | 5 mV   |
| Amplitude              | 25 mV  |

Table 2. Speciation of  $\Gamma$  (nM) by CSV using the silver-amalgam electrode in water samples collected from the estuary (7 stations) of the river Mersey and Liverpool Bay (England) by the proposed method. The iodide concentration was measured using the recommended procedure. Two samples were acidified to pH 2 and treated with ascorbic acid (0.5 mM) to obtain the concentration of iodate (corrected for the initial iodide).

| Station       | Salinity | $\Gamma$ (nM) | $\text{IO}_3^-$ (nM) | Total $\Gamma$ (nM) |
|---------------|----------|---------------|----------------------|---------------------|
| 1             | 19       | $72 \pm 3$    | $96 \pm 3$           | $168 \pm 1$         |
| 2             | 20       | $137 \pm 3$   | -                    | -                   |
| 3             | 22       | $170 \pm 10$  | -                    | -                   |
| 4             | 26       | $252 \pm 13$  | -                    | -                   |
| 5             | 29       | $233 \pm 4$   | -                    | -                   |
| 6             | 31       | $158 \pm 10$  | -                    | -                   |
| Liverpool Bay | 32       | $183 \pm 4$   | $250 \pm 9$          | $433 \pm 8$         |

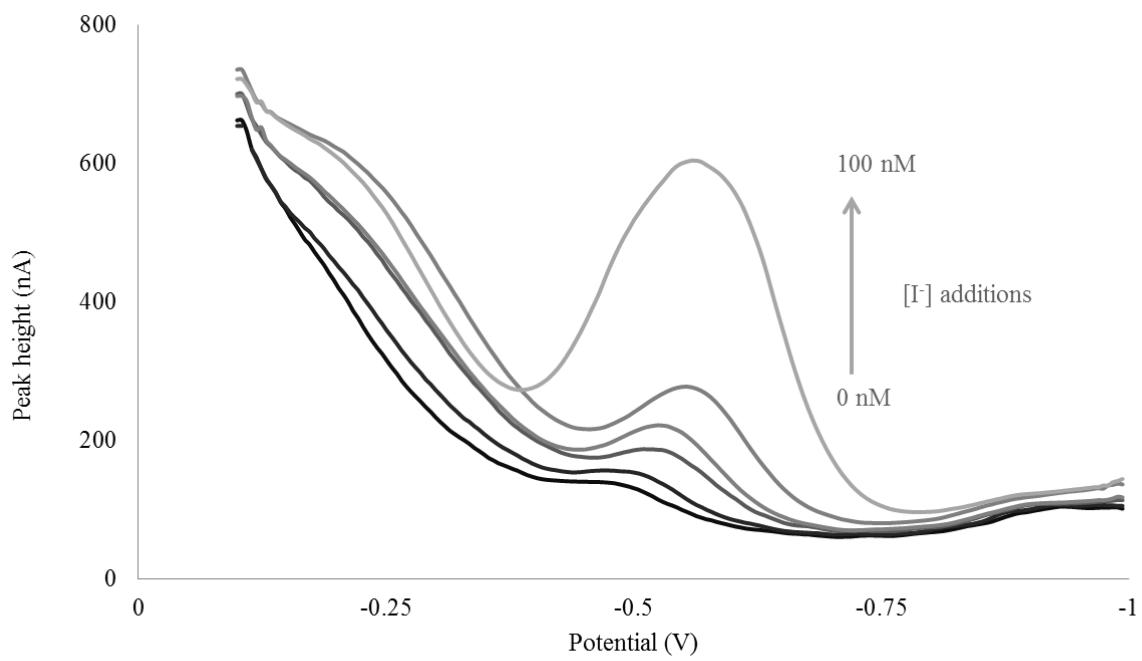


Figure 1

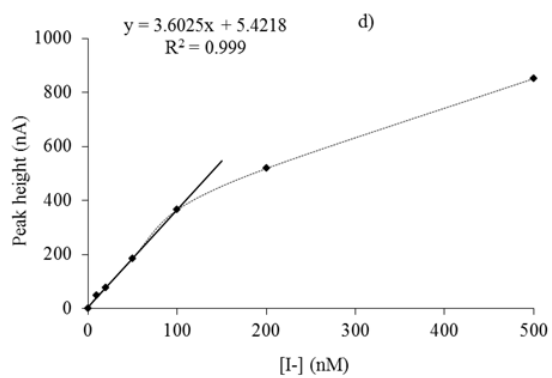
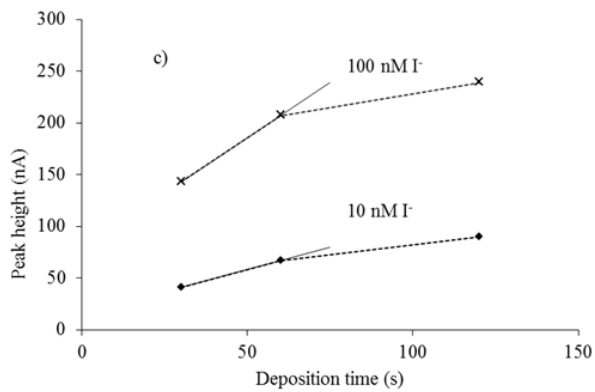
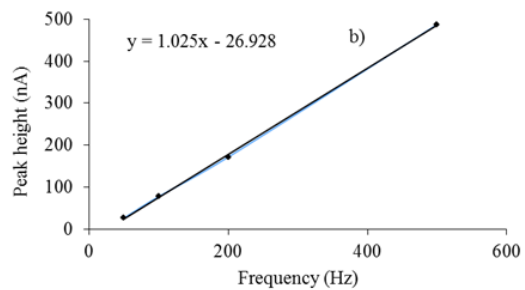
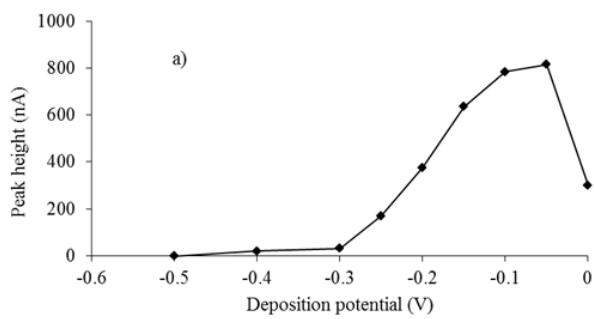


Figure 2