

## Determination of heavy metals in root crops using bismuth nanoparticles modified graphene paste electrode

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**Abstract.** Electrochemical detection of lead ( $\text{Pb}^{2+}$ ) and cadmium ( $\text{Cd}^{2+}$ ) was accomplished via anodic stripping voltammetry (ASV) using bismuth nanoparticle (BiNP) modified graphene paste electrode (GPE). The electrode was fabricated by mixing bismuth nanoparticles, graphene, and mineral oil and the mixture was packed in a Teflon syringe. The best electrode was determined by varying the amount of BiNP while the amount of graphene and mineral oil were kept constant at 0.21 g and 0.80  $\mu\text{L}$ , respectively. The highest peak currents were obtained using 1.5 mg BiNP modified GPE. The ASV parameters, namely accumulation time, deposition time, and accumulation potential, were optimized. The calibration curve, analytical sensitivity, limit of detection (LOD), and limit of quantitation (LOQ) of the optimized electrode were determined. The correlation values for  $\text{Pb}^{2+}$  ( $R^2 = 0.9409$ ) and  $\text{Cd}^{2+}$  ( $R^2 = 0.9086$ ) in the calibration curves showed a positive linear relationship between the anodic peak current and heavy metal concentration. The LOD for both  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  is found to be 100 ppb. The application of the modified electrode on real sample analysis was performed using root crops purchased from local supermarkets. According to ASV and AAS analyses, most of the samples contained  $\text{Cd}^{2+}$  while only a few contained  $\text{Pb}^{2+}$ . Other metals, such as  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$ , were also detected via ASV.

**Key words:** bismuth nanoparticles, graphene, heavy metals, root crops, voltammetry.

## INTRODUCTION

Root crops are one of the most important crops in the Philippines. These are plant roots which can be consumed for they are rich in carbohydrates and dietary fiber which make them a good alternative to rice. The demand for rice increases in the Philippines which makes its price increase as well. This makes root crops such as cassava (*Manihot esculenta*), potato (*Solanum tuberosum*), purple yam (*Dioscorea alata*), sweet potato (*Ipomoea batatas*), and taro (*Colocasia esculenta*) cheaper alternatives to rice. In addition, cassava, in particular, contributes less fat which suggests that this root crop can be used as an alternative to rice by reducing the risk of diabetes of the consumer (Nwose et al., 2017). Potatoes and purple yams are both rich in vitamins B6 and C. Sweet potatoes help in maintaining the blood sugar levels of the body. Taro has vitamins B, C and E. It also has a low content of saturated fat, cholesterol, and sodium (Pereira et al., 2015).



Commercially available root crops are those grown conventionally in farms. Toxic pesticides used to control insects and weeds on these crops contain toxic chemicals that are absorbed through the soil, making them harmful to the environment. These pesticides significantly increase the heavy metal content of plants, especially Lead ( $\text{Pb}^{2+}$ ), Copper ( $\text{Cu}^{2+}$ ), and Cadmium ( $\text{Cd}^{2+}$ ) (Chiroma et al., 2007). Aside from this, root crops can also be contaminated through the accumulation of heavy metals in the atmosphere due to industrialization, urbanization, and deforestation. Previous researchers have investigated the presence of heavy metal concentrations in soils and vegetation within the urban areas of the Philippines (Navarrete et al., 2017).

According to the World Health Organization (WHO) and the Commission of the European Communities (CEC), the permitted threshold of Cadmium for stem and root vegetables are 0.1 ppm, but the permissible limit of Cadmium for plants, in general, is about 0.02 ppm. For Lead, the limit for metal content within plants is 2 ppm. These limitations were measured to monitor the amount of heavy metals people consume from food (Nazir et al., 2015).

Heavy metals are ingested in the body through eating and drinking contaminated foods and drinks and inhaling dust. As a result, they impose a serious health risk on the person by affecting the central nervous system, and the vital organs. In addition to this, heavy metal accumulation in the human body has long-term effects, which include degenerative diseases like cancer and Alzheimer's disease (Chen et al., 2016). As a result, the need of detecting heavy metals in the environment increases. There are various analytical methods that can be done to detect heavy metals, namely, Atomic Absorption Spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), Time-of-Flight Mass Spectrometry (TOFMS), and Microwave Plasma-Atomic Emission Spectrometry (MP-AES). However, these methods are complicated and require expensive machines.

The electrochemical detection of heavy metals offers several advantages such as its high sensitivity, cost-effectiveness, energy-saving, high resolution, and accuracy compared to the other techniques (Baldigowski, 2011). One of these detection techniques is anodic stripping voltammetry (ASV) which is commonly used due to its high sensitivity in detecting trace metals and its low detection limit. For many years, the most commonly used working electrode in ASV was the Mercury (Hg) electrode which possesses the excellent capability to pre-concentrate heavy metals. However, it is very toxic and requires careful handling. Hence, alternative electrodes such as chemically modified glassy carbon electrodes and carbon paste electrodes are used.

Other materials which have good electrical conductivity can be used as an alternative to Hg. In the detection of trace heavy metals, Bismuth (Bi) is usually used in modifying electrodes because of its inexpensiveness and high sensitivity. Compared to Hg electrodes, it is safer to use because it is non-toxic and it has a wider range of potential (Sadok, 2016). Aside from this, it has the ability to fuse heavy metals together (Lee et al., 2016). These properties allow Bi modified electrodes to detect various electro-active species simultaneously in a chosen sample. When used in ASV, bismuth can provide accurate, sharp, and well defined current peaks. Hence, these sharp outcomes allow the users to identify and quantify the metals present in the sample in a quick and reliable manner (Baron-Jaimez et al., 2013).



Graphene is a carbon-based conductive material that is commonly used as an electrode substrate. Its molecular structure consists of a six-membered aromatic ring with sp<sup>2</sup> bonds on the carbons. The chemical properties of graphene include wide potential window and low background current (Li & Miao, 2013). Even though it is the lightest material known, it is very strong and dense (Ghany et al., 2017).

For decades, the most popular electrode material, carbon paste, was commonly used for the construction of different electrodes, sensors, and detectors (Vytras et al., 2009). Compared to other electrodes, carbon paste electrodes do not need any pretreatment (Olson & Adams, 1960). The universal applicabilities of the carbon paste express the specific properties and the versatility of electrode material together with advanced technology. This kind of adaptability from the electrode material is described to be the most distinguishable feature conveyed by modern electrochemistry with carbon paste-based electrodes in comparison to the past ones (Zima et al., 2009).

In this study, bismuth nanoparticle modified graphene paste electrodes (BiNP/GPE) were fabricated and were used as the working electrode in anodic stripping voltammetry (ASV) for the detection of heavy metals, mainly lead and cadmium, in commercial root crops from local supermarkets.

## **MATERIALS AND METHODS**

### **Chemicals and reagents**

Graphene nanopowder (multilayer graphene; average flake thickness: 60 nm) was purchased from Graphene Supermarket (Calverton, NY, USA). Bismuth nanopowder (< 100 nm particle size), sodium chloride, lead chloride, cadmium chloride, copper chloride, mineral oil, and nitric acid were purchased from Sigma, Aldrich (Sigma-Aldrich Pte Ltd, Singapore).

### **Glassware and equipment**

The following are the equipment used in this study: BOSCH SAE200 electronic balance, BANDELIN SONOREX sonicator bath, Autolab PGSTAT128N potentiostat, Transferette® micropipette, agate mortar and pestle, AA-6300 Shimadzu atomic absorption spectrophotometer, spatula, crucible, Thermolyne 48000 furnace, La Germania general heat hot plate and glassware such as beakers, petri dish, and graduated cylinder.

### **Fabrication of BiNP modified graphene paste electrode**

The graphene paste was prepared by mixing the graphene powder, bismuth nanopowder, and mineral oil together using agate mortar and pestle for a total of 30 minutes. The amount of graphene was 0.21 grams, which was kept constant for all of the fabricated GPE. The resulting paste was transferred to a Teflon syringe whose end was cut open to serve as its holder. All the fabricated electrodes maintained the same height (2 cm) of the graphene mixture. The diameter of the syringe opening is 3 mm. A copper wire with a diameter of 1 mm was then inserted into the GPE to obtain an ohmic contact. The electrode surface exposed to the electrolyte solution was rubbed on a qualitative filter paper to give it a smooth finish before use.



### **BiNP amount optimization**

The amount of BiNP used was optimized in order to determine the best electrode to be used in detecting 10 ppm each of  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ . The Bi was varied from 0 to 3.0 mg with 0.5 mg increments. The amounts of mineral oil and graphene powder were kept constant at 0.80  $\mu\text{L}$  and 0.21 g, respectively. Thus, the corresponding BiNP:graphene:mineral oil ratios are 70.35:0.10:29.55, 82.60:0.06:17.35, 87.68:0.04:12.28, 90.47:0.03:9.50, 92.23:0.03:7.75, and 93.44:0.02:6.54.

### **Preparation of Stock Solutions**

Stoichiometry was calculated in order to obtain the actual concentration of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions since only  $\text{CdCl}_2$  and  $\text{PbCl}_2$  were available in the laboratory. First, the gravimetric factor was calculated by dividing the molar mass of the single element over the molar mass of the compound. Then, the amount of  $\text{PbCl}_2$  and  $\text{CdCl}_2$  was calculated to obtain a 10 ppm solution of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  in a 100 mL deionized water. For the optimization of the ASV parameters, 1.6 mg of  $\text{CdCl}_2$ , and 1.3 mg of  $\text{PbCl}_2$  with 0.5844 g of NaCl (0.1 M NaCl) was used to obtain a solution containing 10 ppm of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ .

To obtain the calibration curves of each heavy metal, 10 ppm stock solution of  $\text{CdCl}_2$  and  $\text{PbCl}_2$  was utilized. Aliquots of the stock solution were then mixed with a 0.1 M NaCl solution to obtain a final volume of 100 mL. Six solutions were used for the calibration curve: 100 ppb, 200 ppb, 300 ppb, 400 ppb, 500 ppb, and 600 ppb. The outcome solution was utilized in retrieving the calibration curves.

### **Anodic Stripping Voltammetry**

An AUTOLAB potentiostat/galvanostat was used for the measurements made in ASV. The fabricated BiNP/ GPE (working electrode), Ag/AgCl electrode (reference electrode), and platinum coil (counter electrode) was placed in the voltammetric cell. The solution in the voltammetric cell was made of 0.5844 NaCl and 100 mL deionized water. Lead and cadmium were detected simultaneously. In order to obtain the concentrations of the heavy metals in the real samples, the equation for the calibration curve for each heavy metal was used.

After each ASV run, the electrode underwent cleaning by applying a -0.95 V of potential for 15 minutes in order to remove the heavy metals from the surface of the electrode back to the used analyte.

### **Real Sample Analysis**

The real samples underwent wet and dry ashing. The commercial root crop samples were cassava, potato, purple yam, sweet potato, and taro. Two sets of samples were analyzed: one from Divisoria Supermarket and the other from Balintawak Supermarket. The skin and flesh of the samples were tested separately.

One gram of each sample was placed in a crucible. Then, the crucible was transferred in a furnace, which has a temperature of 450  $^{\circ}\text{C}$ . The obtained white colored ash was mixed with 2 mL of concentrated nitric acid. It was then placed on a hot plate until it was almost dry. Finally, it was cooled to room temperature before it was added to the electrolyte solution.



### Atomic Absorption Spectrometry

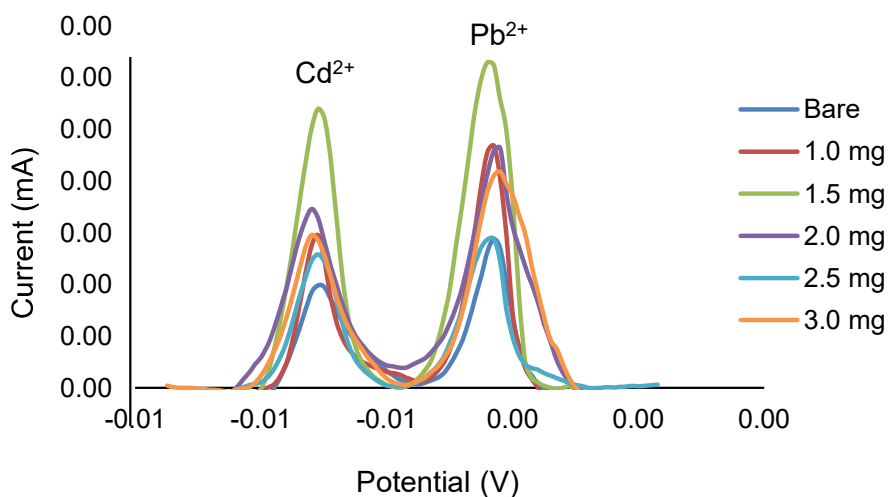
The results from the ASV were verified using AAS. The equipment for AAS was the AA-6300 Shimadzu Atomic Absorption Spectrophotometer apparatus. Seven stock solutions were prepared: 100 ppb, 200 ppb, 300 ppb, 400 ppb, 500 ppb, and 600 ppb. These concentrations were also tested for the calibration curve using ASV. The solutions that were used to calibrate the electrode for ASV was also used for AAS calibration. The calibration curve that was obtained was used to determine the concentrations of the heavy metals in the real samples.

## RESULTS AND DISCUSSION

### Determination of the Best Electrode

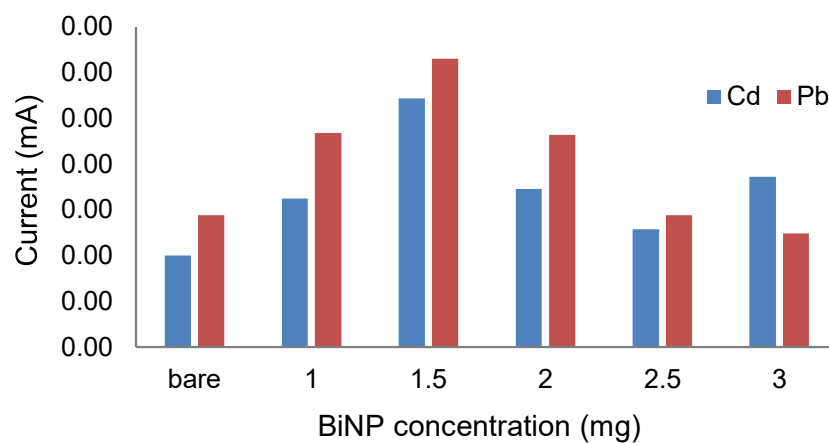
The optimization of the electrodes was accomplished by varying the amount of BiNP in 6 electrodes, which ranged from 0 mg to 3.0 mg of BiNP. The amount of mineral oil and graphene were held constant in all of the electrodes. Then, the fabricated electrodes were used to detect 10 ppm stock solution of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  using the same ASV recipe. Consequently, 10 ppm was utilized as the standard solution for optimization to be able to discern the voltammetric peaks.

In the simultaneous detection of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , the highest peak current was obtained with the electrode modified with 1.5mg of BiNP (Fig. 1 and Fig. 2). The voltammograms (Fig. 3 and Fig. 5) and their corresponding bar graphs (Fig. 4 and Fig. 6) indicate that the highest peak for the sequential detection of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were both obtained with 1.5 mg BiNP. Since the GPE modified with 1.5 mg BiNP exhibited the highest anodic peak currents in both simultaneous and sequential detection, it was chosen as the best electrode. In addition, it was shown that as the BiNP increased, the modified electrode was able to detect more lead than cadmium compared to the lesser concentrations of BiNP. At higher Bi concentrations, bismuth will hold the target metals, and affect the voltammetric peaks of the heavy metals (Barón-Jaimez et al., 2014). It was suggested that lower concentrations of BiNP are more sensitive towards lead.

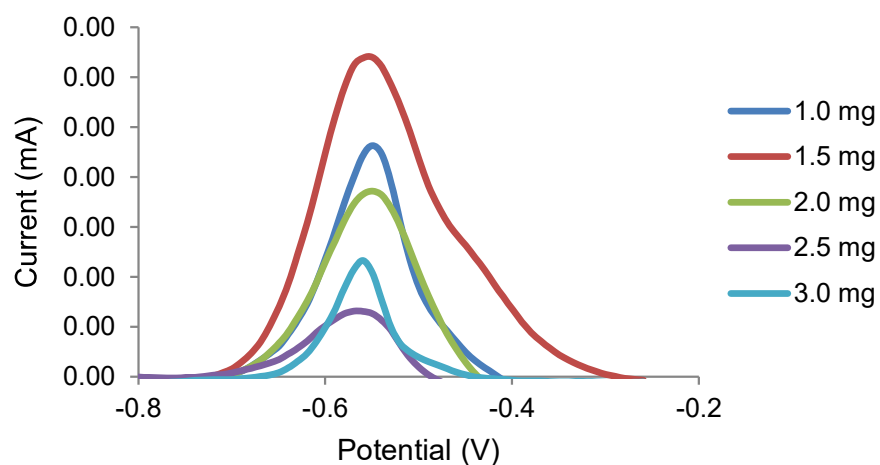


**Figure 1.** Anodic Stripping Voltammograms for varying BiNP amount for the simultaneous detection of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ .

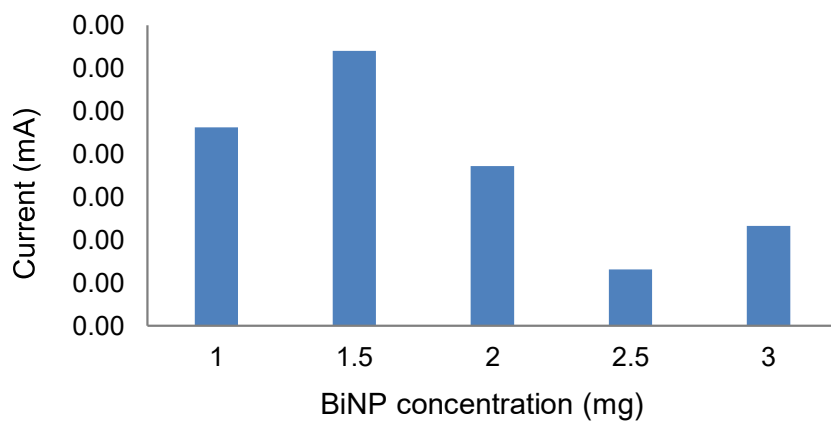




**Figure 2.** Anodic current peaks for varying BiNP amount for the simultaneous detection of Pb<sup>2+</sup> and Cd<sup>2+</sup>.

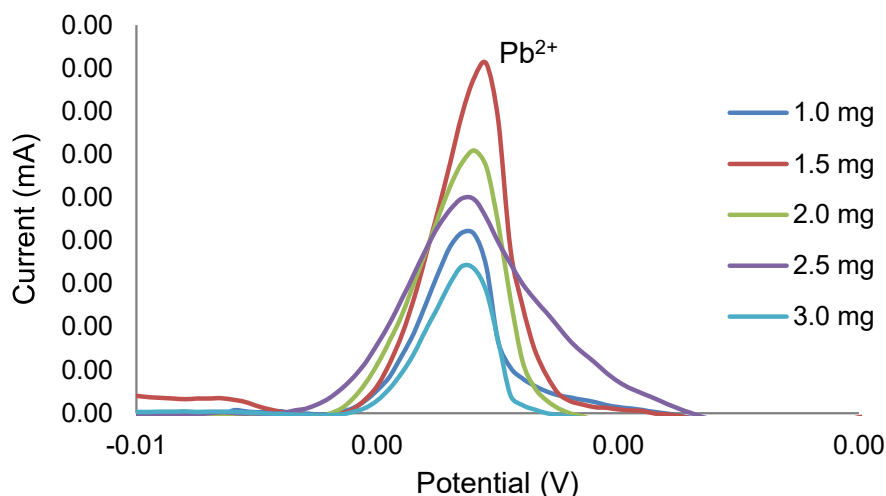


**Figure 3.** Anodic Stripping Voltammograms of Cd<sup>2+</sup> detection using BiNP GPE modified electrodes with varying amounts of BiNP.

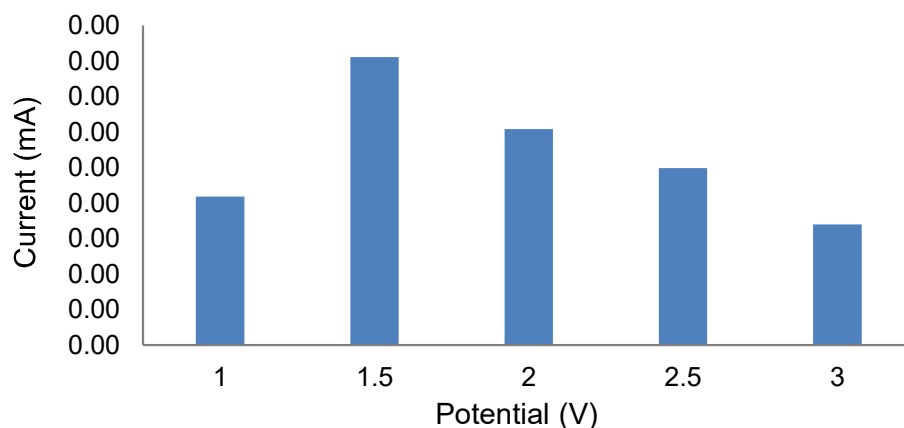


**Figure 4.** Anodic current peaks for varying BiNP for the sequential detection of Cd<sup>2+</sup>.





**Figure 5.** Anodic Stripping Voltammograms of  $\text{Pb}^{2+}$  detection using BiNP GPE modified electrodes with varying amounts of BiNP.



**Figure 6.** Anodic current peaks for varying BiNP for the sequential detection of  $\text{Pb}^{2+}$ .

### Optimized Electrode

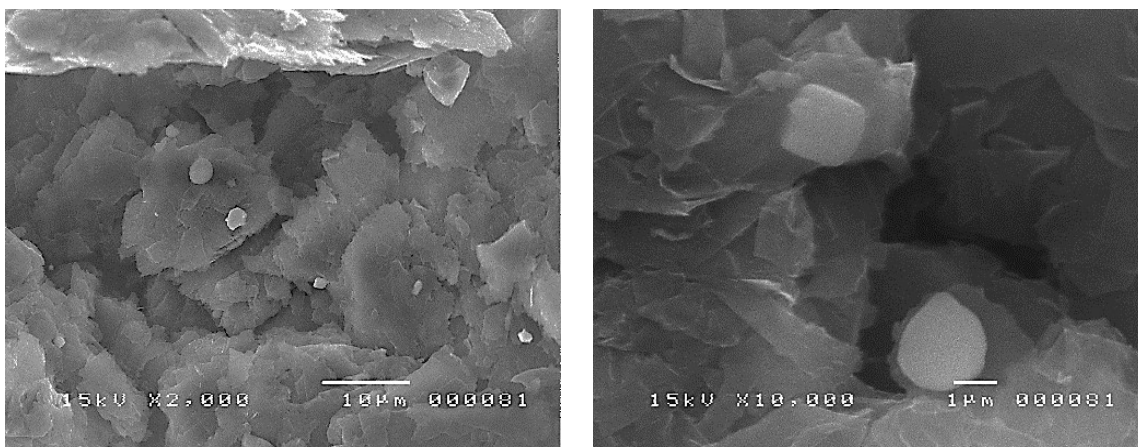
It can be deduced from the obtained results of BiNP optimization that the best electrode has 1.5 mg of BiNP. The addition of the BiNP to the electrode enhanced its sensitivity and selectivity in detecting the heavy metals in a solution due to its ability to form ‘fused’ alloy with  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . This formation is accountable for the exceptional voltammetric performance of bismuth modified electrodes (Yang et al., 2014). Also, the large surface area of the BiNP along with the high conductivity of the graphene makes the BiNP GPE a sensitive electrode for the detection of heavy metals (Niu et al., 2015).

### Characterization of the best electrode:

#### Scanning Electron Microscopy (SEM)

The morphological structures of the graphene nanoparticles, Bismuth Nanoparticles, and the best electrode were analyzed by SEM. The obtained images show that the graphene has a flaky appearance, while the Bismuth was globular in shape (Fig. 7).





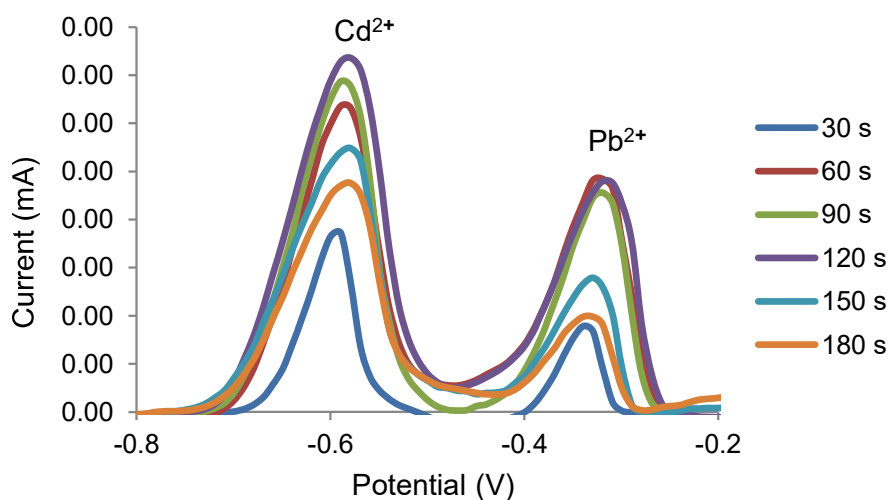
**Figure 7.** Scanning Electron Microscopy images of BiNP GPE.

### ASV Parameters Optimization

In order to get the highest peak currents for the best electrode, the parameters in ASV were varied namely the accumulation time, deposition time, and accumulation potential. The best electrode was utilized to detect  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in the stock solution. The accumulation time and deposition time were varied from 30 s to 180 s with increments of 30 s. The accumulation potential was varied from -0.8 V to -1.0 V increments of -0.05 V.

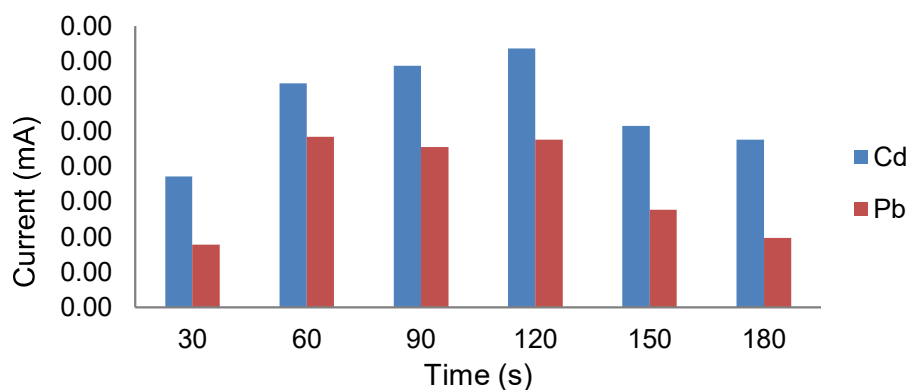
### Accumulation Time

Based on the voltammograms (Fig. 8) and the corresponding histogram (Fig. 9), the peak current increased as the accumulation time increased. The peak gradually decreased after 120 s. Thus, 120 s was the optimum accumulation time.



**Figure 8.** Anodic Stripping Voltammograms for the accumulation time of 10 ppm  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from 30 s to 180 s.

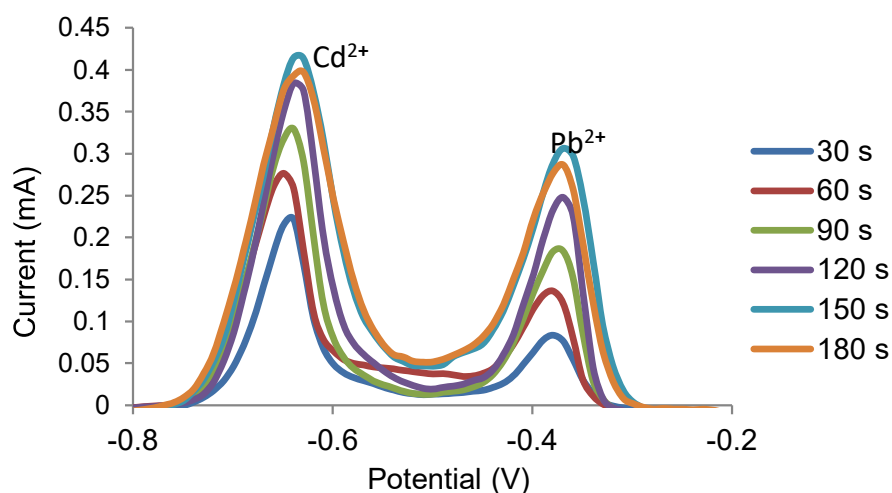




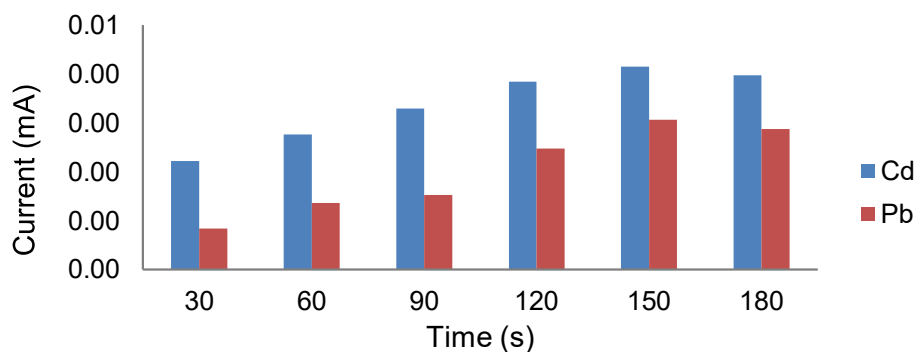
**Figure 9.** Accumulation time anodic current peaks for the simultaneous detection of 10 ppm  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from 30 s to 180 s.

### Deposition Time

The voltammograms (Fig. 10) and corresponding histogram (Fig. 11), indicate that the current peak increased as the deposition time increased. Thus, the optimum deposition time is 150 s.



**Figure 10.** Anodic Stripping Voltammograms for the deposition time of 10 ppm of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from 30 s to 180 s.

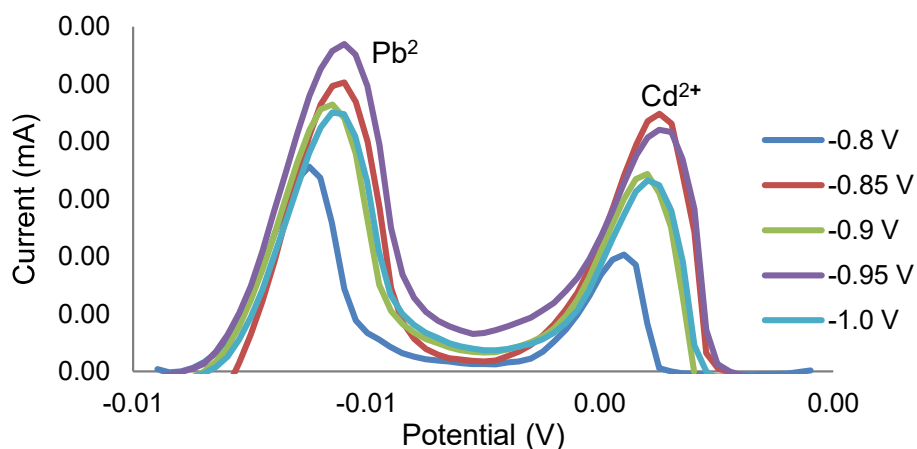


**Figure 11.** Deposition time anodic current peaks for the simultaneous detection of 10 ppm  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from 30 s to 180 s.

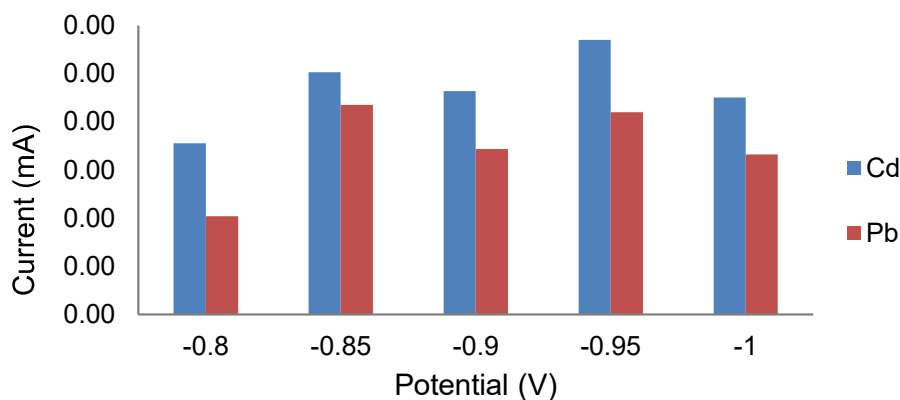


### Accumulation Potential

As illustrated in the voltammograms (Fig. 12) and the corresponding bar graph (Fig. 13), the highest peak was obtained at -0.95 V. Hence, the accumulation potential of -0.95 V is the optimum accumulation potential.



**Figure 12.** Anodic Stripping Voltammograms for the accumulation time of 10 ppm of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from -0.80 V to -1.0 V.



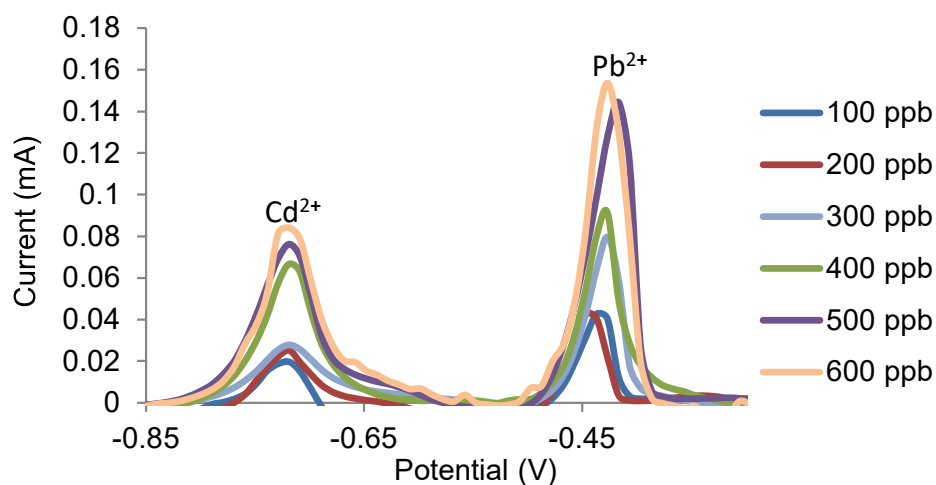
**Figure 13.** Accumulation potential anodic current peaks of 10 ppm of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from -0.80 V to -1.0 V.

### Calibration Curve

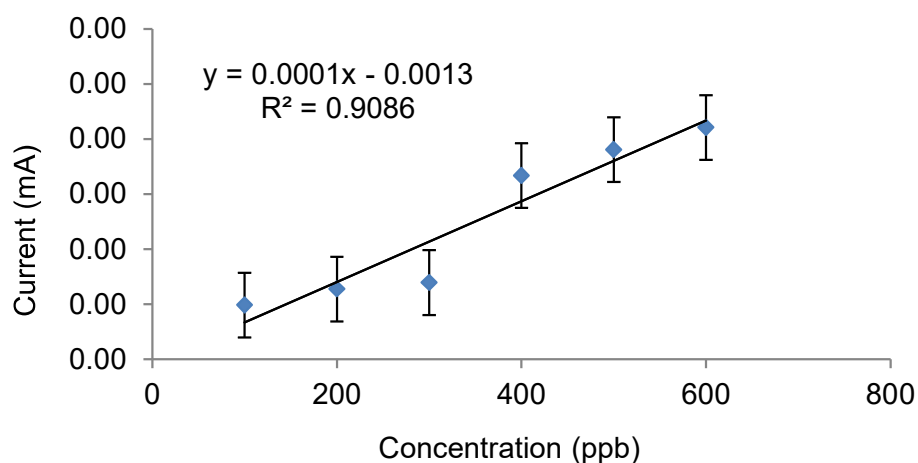
The calibration curve of the best electrode was obtained by varying the concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from 100 ppb to 600 ppb with increments of 100 ppb. Fig. 14 shows the ASV curves for varying concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . For each heavy metal, the resulting current peaks were plotted against their respective concentrations (Fig. 15 and Fig. 16).

The  $R^2$  value for Pb and Cd are 0.9409 and 0.9086, respectively. These values are close to 1, which indicates that there is a positive linear relationship between the peak current and the heavy metal concentration. It can also be seen from Figs 16 and 17 that the 1.5 mg BiNP modified GPE can detect concentrations as low as 100 parts per billion of both  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ .

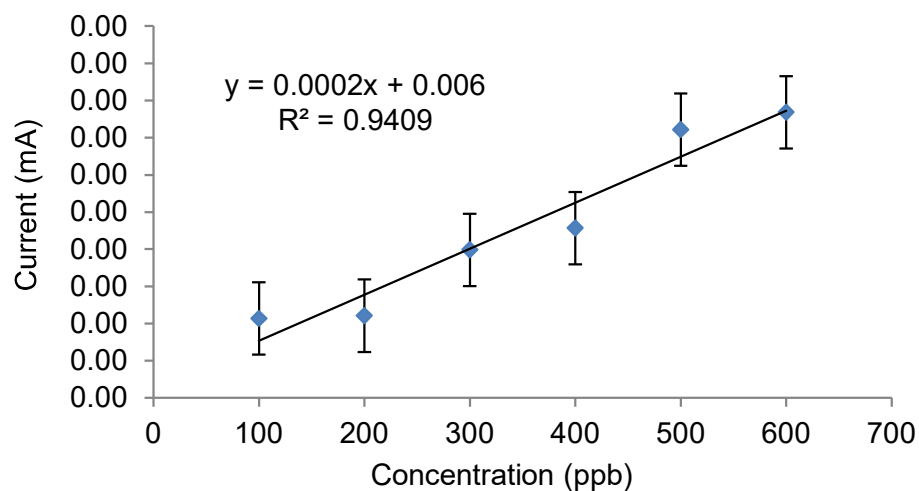




**Figure 14.** Anodic Stripping Voltammograms for various concentrations of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ .



**Figure 15.** ASV Calibration curve for  $\text{Cd}^{2+}$  using the optimized BiNP GPE electrode.



**Figure 16.** ASV Calibration curve for  $\text{Pb}^{2+}$  using the optimized BiNP GPE electrode.



### Limit of Detection and Limit of Quantitation

The theoretical limit of detection and limit of quantitation of the best electrode were calculated to determine the minimum concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  that the BiNP GPE can detect. The experimental LOD values were lower compared to the theoretical values. As seen in Table 1, the lowest concentrations that can be detected is 100 ppb for both Cd and Pb.

**Table 1.** Limit of Detection and Limit of Quantitation

|    | Experimental<br>LOD (ppb) | Theoretical<br>LOD (ppb) | LOQ<br>(ppb) |
|----|---------------------------|--------------------------|--------------|
| Cd | 100                       | 218.93                   | 663.42       |
| Pb | 100                       | 172.92                   | 523.99       |

### Real Sample Analysis

The real sample analysis for this study was done via anodic stripping voltammetry using the 1.5 mg BiNP modified GPE, and the optimized recipe with 120 s accumulation time, 150 s deposition time, and -0.95 V initial potential.

The amount of Cd and Pb detected from ASV in the samples are shown in Table 2. Those labeled with 'SB' are the skin of the root crops from Balintawak. Those labeled with 'SD' are the skins of the root crops from Divisoria. For those labeled with 'FB' and 'FD', these are the inner part of the root crops from Balintawak and Divisoria, respectively. The modified electrode was able to detect most of the cadmium content in all the samples except for Taro- FB, and Purple Yam-SD. However, lead was detected in less than half of the samples.

**Table 2.** Cd and Pb concentrations detected via ASV

| CADMIUM (ppb)   |        | LEAD (ppb)      |       |
|-----------------|--------|-----------------|-------|
| Potato-SB       | 339.47 | Potato-SB       | N.D.  |
| Potato-SD       | 68.71  | Potato-SD       | N.D.  |
| Potato-FB       | 41.99  | Potato-FB       | N.D.  |
| Potato-FD       | 58.93  | Potato-FD       | N.D.  |
| Sweet Potato-SB | 52.61  | Sweet Potato-SB | N.D.  |
| Sweet Potato-SD | 18.99  | Sweet Potato-SD | 25.06 |
| Sweet Potato-FB | 32.68  | Sweet Potato-FB | 43.40 |
| Sweet Potato-FD | 116.32 | Sweet Potato-FD | 79.48 |
| Taro-SB         | 270.55 | Taro-SB         | N.D.  |
| Taro-SD         | 143.81 | Taro-SD         | N.D.  |
| Taro-FB         | N.D.   | Taro-FB         | 47.12 |
| Taro-FD         | 42.55  | Taro-FD         | 28.21 |
| Purple Yam-SB   | 112.78 | Purple Yam-SB   | N.D.  |
| Purple Yam-SD   | N.D.   | Purple Yam-SD   | N.D.  |
| Purple Yam-FB   | 69.15  | Purple Yam-FB   | N.D.  |
| Purple Yam-FD   | 197.13 | Purple Yam-FD   | 44.67 |
| Cassava-SB      | 623.70 | Cassava-SB      | N.D.  |
| Cassava-SD      | 276.72 | Cassava-SD      | 24.27 |
| Cassava-FB      | 385.64 | Cassava-FB      | N.D.  |
| Cassava-FD      | 104.70 | Cassava-FD      | 53.22 |



Evidently, Cassava-SB has the highest cadmium concentration with the amount of 385.64 ppb, while Sweet Potato- SD has the lowest cadmium concentration of 18.99 ppb. For the lead concentration, Sweet Potato-FD has the most amount with a concentration of 79.48 ppb, while Cassava- SD had the least amount with a concentration of 24.27 ppb. For the samples that are labeled with N.D. (Not Detected), their concentrations are below the detection limit of the optimized electrode.

### Atomic Absorption Spectroscopy

Atomic Absorption Spectrometry was used to verify the results obtained from the ASV. The cadmium and lead concentrations detected from AAS can be seen in Table 3. For the cadmium concentration, Purple Yam- SB with a concentration of 37.92 ppb has the highest amount, while Sweet Potato-FB with a concentration of 6.66 ppb has the lowest amount. For lead, only five samples were detected, Potato- FB, Purple Yam-SB, Purple Yam-FB, Cassava- SB, and Cassava- FB. The sample with the most amount of lead was Purple Yam- SB with the concentration of 141.58 ppb, and the least amount of lead was Potato- FB with a concentration of 2.57 ppb. For samples with a concentration that are not detected (N.D.), their concentrations are below the detection limit of AAS.

**Table 3.** Cd and Pb concentrations detected via AAS

| CADMIUM (ppb)   |         | LEAD (ppb)      |        |
|-----------------|---------|-----------------|--------|
| Potato-SB       | 10.71   | Potato-SB       | N.D.   |
| Potato-SD       | 23.16   | Potato-SD       | N.D.   |
| Potato-FB       | 17.08   | Potato-FB       | N.D.   |
| Potato-FD       | 25.18   | Potato-FD       | 2.57   |
| Sweet Potato-SB | 14.76   | Sweet Potato-SB | N.D.   |
| Sweet Potato-SD | 20.26   | Sweet Potato-SD | N.D.   |
| Sweet Potato-FB | 6.66    | Sweet Potato-FB | N.D.   |
| Sweet Potato-FD | 29.24   | Sweet Potato-FD | N.D.   |
| Taro-SB         | 32.99   | Taro-SB         | N.D.   |
| Taro-SD         | 18.53   | Taro-SD         | N.D.   |
| Taro-FB         | 32.99   | Taro-FB         | N.D.   |
| Taro-FD         | 13.32   | Taro-FD         | N.D.   |
| Purple Yam-SB   | 37.92   | Purple Yam-SB   | 141.58 |
| Purple Yam-SD   | 27.49   | Purple Yam-SD   | N.D.   |
| Purple Yam-FB   | 33.87   | Purple Yam-FB   | N.D.   |
| Purple Yam-FD   | 26.92   | Purple Yam-FD   | 10.29  |
| Cassava-SB      | 34.16   | Cassava-SB      | 46.34  |
| Cassava-SD      | 20.84   | Cassava-SD      | N.D.   |
| Cassava-FB      | 24.3153 | Cassava-FB      | 10.297 |
| Cassava-FD      | 30.39   | Cassava-FD      | N.D.   |

### Comparison of ASV and AAS results

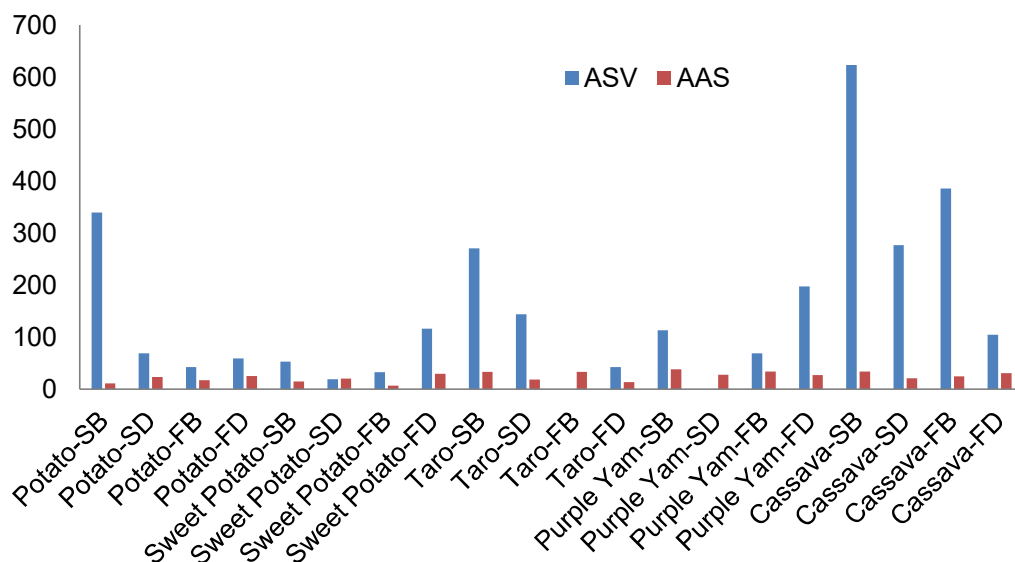
Based on the data from both ASV and AAS (Table 4), the majority of the samples contained small concentrations of cadmium in both the skin and flesh. Lead was also detected in some samples. However, the voltammograms from the ASV show that more cadmium was detected compared to AAS. According to WHO, the permissible intake



limit for Cd is 100 ppb and 2 ppm for  $Pb^{2+}$ . For cadmium, nine samples exceeded the limit according to the results obtained from ASV: sweet potato-FD, taro-SB, taro-SD, purple yam-SB, purple yam-FD, cassava-SB, cassava-SD, cassava-FB, and cassava-FD. According to ASV, the lead concentrations in some of the samples were below the WHO limit. Since both the skin and flesh of the root crops contain trace heavy metals, the root crops possibly absorbed them from contaminated soil or irrigation water. Aside from  $Cd^{2+}$  and  $Pb^{2+}$ , the BiNP GPE was also able to detect iron ( $Fe^{3+}$ ) and copper ( $Cu^{2+}$ ). However, the concentrations of the said metals were not determined since the electrode was calibrated for Cd and Pb only. Fig. 17 and Fig. 18 are the corresponding bar graphs for Table 4.

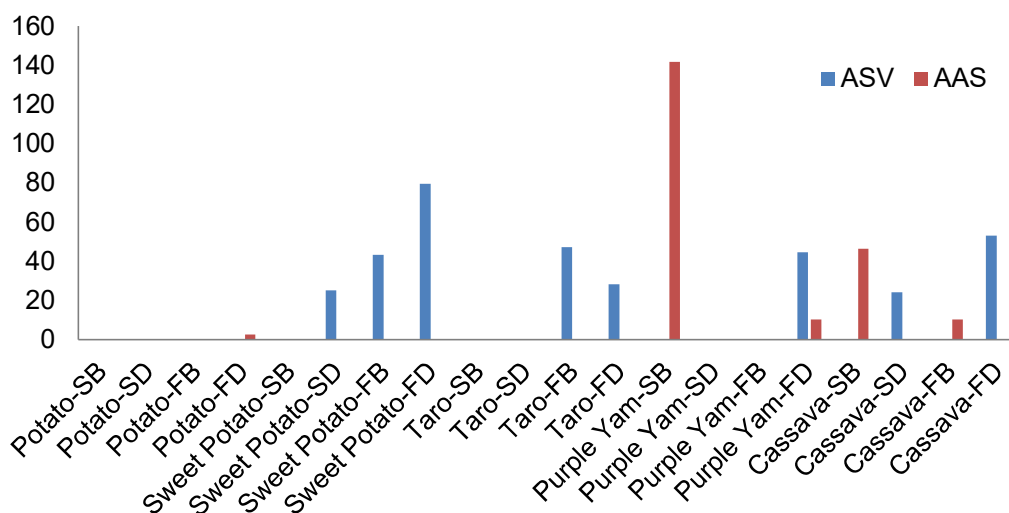
**Table 4.** Comparison of ASV and AAS Results

| Sample          | CADMIUM   |           | LEAD      |           |
|-----------------|-----------|-----------|-----------|-----------|
|                 | ASV (ppb) | AAS (ppb) | ASV (ppb) | AAS (ppb) |
| Potato-SB       | 339.47    | 10.71     | N.D.      | N.D.      |
| Potato-SD       | 68.71     | 23.16     | N.D.      | N.D.      |
| Potato-FB       | 41.99     | 17.08     | N.D.      | N.D.      |
| Potato-FD       | 58.93     | 25.18     | N.D.      | 2.57      |
| Sweet Potato-SB | 52.61     | 14.76     | N.D.      | N.D.      |
| Sweet Potato-SD | 18.99     | 20.26     | 25.06     | N.D.      |
| Sweet Potato-FB | 32.68     | 6.66      | 43.40     | N.D.      |
| Sweet Potato-FD | 116.32    | 29.24     | 79.48     | N.D.      |
| Taro-SB         | 270.55    | 32.99     | N.D.      | N.D.      |
| Taro-SD         | 143.81    | 18.53     | N.D.      | N.D.      |
| Taro-FB         | N.D.      | 32.99     | 47.12     | N.D.      |
| Taro-FD         | 42.55     | 13.32     | 28.21     | N.D.      |
| Purple Yam-SB   | 112.78    | 37.92     | N.D.      | 141.58    |
| Purple Yam-SD   | N.D.      | 27.50     | N.D.      | N.D.      |
| Purple Yam-FB   | 69.15     | 33.87     | N.D.      | N.D.      |
| Purple Yam-FD   | 197.13    | 26.92     | 44.67     | 10.29     |
| Cassava-SB      | 623.70    | 34.16     | N.D.      | 46.34     |
| Cassava-SD      | 276.72    | 20.84     | 24.27     | N.D.      |
| Cassava-FB      | 385.64    | 24.31     | N.D.      | 10.30     |
| Cassava-FD      | 104.70    | 30.39     | 53.22     | N.D.      |



**Figure 17.** Bar graph of the amount of cadmium detected from the root crops via ASV and AAS.





**Figure 18.** Bar graph of the amount of lead detected from the root crops via ASV and AAS.

## CONCLUSIONS

The fabricated BiNP GPE was shown to be effective in detecting  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ . It is evident that the addition of BiNP improved the sensitivity of the GPE. Out of the six electrodes with different amounts of BiNP, the electrode with 1.5 mg BiNP exhibited the highest anodic current peaks for both the simultaneous and sequential detection of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . Scanning electron microscopy analyses confirmed the presence of BiNP and graphene in the fabricated electrode. The calibration curves obtained showed a strong linear relationship from 100 ppb to 600 ppb for both  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . The LOD of the optimized modified electrode was found to be 100 ppb for both  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . Real sample analysis showed that majority of the samples contained small concentrations of cadmium in both the skin and flesh. Lead was also detected in some samples.

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