



# Advanced electrochemical detection of arsenic using platinum-modified boron-doped diamond by anodic stripping voltammetry

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## ABSTRACT

**Background:** Platinum-modified boron-doped diamond (BDD) electrodes were effectively fabricated through wet seeding and electrodeposition combination techniques. **Methods:** This research involved the utilization of various chemicals and apparatus, the modification of boron-doped diamond (BDD) electrodes with platinum using wet seeding and electrodeposition, and the detection of  $\text{As}^{3+}$  and  $\text{As}^{5+}$  using a phosphate buffer solution and anodic stripping voltammetry (ASV). **Findings:** Characterization using Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) confirmed the successful deposition of 1.54% platinum on the BDD surface. The altered electrodes was employed as sensors for arsenic species ( $\text{As}^{3+}$  and  $\text{As}^{5+}$ ) using anodic stripping voltammetry (ASV) in a 0.1 M phosphate buffer solution at pH 6. Under optimal conditions, including a deposition potential of -500 mV, a deposition time of 150 s, and a scan rate of 200 mV/s, the linear detection of  $\text{As}^{3+}$  and  $\text{As}^{5+}$  was achieved within a concentration range of 0 to 100 ppb ( $R^2 = 0.9797$  and 0.9903, respectively). Prior to ASV detection of  $\text{As}^{5+}$ , a pretreatment step involving the addition of 0.1 M  $\text{NaBH}_4$  was necessary to reduce  $\text{As}^{5+}$  to  $\text{As}^{3+}$ . The detection limits for  $\text{As}^{3+}$  and  $\text{As}^{5+}$  were determined to be 16.50 ppb and 8.19 ppb, respectively. **Conclusion:** This research highlights the potential of BDD/Pt electrodes in environmental monitoring and arsenic detection applications and demonstrates the method's efficacy for the speciation analysis of arsenic species. **Novelty/Originality of this Study:** This research pioneers the use of platinum-modified boron-doped diamond electrodes for the speciation analysis of arsenic, offering a promising new approach for environmental monitoring applications.

**KEYWORDS:** arsenic; anodic stripping voltammetry; modified BDD electrode; platinum.

## 1. Introduction

Arsenic pollution in both groundwater and surface water has become a significant problem because of its detrimental effects on human health and the ecosystem (Verma and Chaurasia, 2024). The main sources of arsenic accumulation are sewage and industrial waste (Hung et al., 2004). The Agency for Toxic Substances and Disease Registry (ATSDR) categorizes arsenic as a No. 2 priority hazard because of the associated health risks (CDC, 2015). There are four different oxidation states for arsenic such as  $\text{As}^{3-}$ ,  $\text{As}^0$ ,  $\text{As}^{3+}$ , and  $\text{As}^{5+}$ . The most common forms of arsenic in nature are  $\text{As}^{3+}$  and  $\text{As}^{5+}$  (Lestarini and Ivandini, 2019; Shah et al., 2010). However, the arsenic exposure can cause acute poisoning and

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even death in high doses, as well as chronic effects such as lungs, pigments, and skin cancer (Baker et al., 2018; Bhat et al., 2022; Martínez-Castillo et al., 2021). Considering the significant health risks posed by arsenic, coupled with its pervasive presence in our environment, the development of reliable and robust detection methods has become an urgent necessity (Baloch et al., 2020).

Fortunately, scientific progress has yielded a range of analytical techniques tailored for this purpose (Bhat et al., 2022; Hung et al., 2004; Rajakovic and Rajakovic-Ognjanovic, 2018). Recently, different procedures and approaches can be utilized to detect arsenic, including titrimetric analysis, spectrophotometry, hydride generation atomic fluorescence spectrometry, chemiluminescence, inductively coupled plasma atomic emission spectrometry, and inductively coupled plasma mass spectrometry (Afkhami et al., 2001; Assegid et al., 2011; Khansili, 2023; Nguyen et al., 2018; Pasha and Narayana, 2008). Nevertheless, those procedures employ rather complicated methods as well as requiring both thorough and costly instrumentation (De Carvalho et al., 2007).

Another method that can be employed with the same efficiency but with the advantage of portability is electrochemistry (Hung et al., 2004; Pramadewandaru et al., 2023; Rajakovic and Rajakovic-Ognjanovic, 2018; Scholz, 2024). Through electrochemical procedures, these techniques hold essential benefits in terms of miniaturization, probability of higher sensitivity, and lower detection limits (Eprilia et al., 2024; Liu et al., 2024). Therefore, electrochemistry is an ideal method for field analysis. Specifically, the stripping voltammetry technique is ideal because it has an advantage in pre-concentration determination, followed by high sensitivity in the stripping process (Alghamdi, 2010; Cavicchioli et al., 2004; Wang et al., 2021).

The cornerstone of this technique lies in the working electrode, which can be fabricated from a variety of materials such as gold (Anggraningrum Ivandini et al., 2012; Babar et al., 2019; Yamada et al., 2008), iridium (Agustiany et al., 2020; L. Chen et al., 2017), silver (Gajdár et al., 2019; Simm et al., 2005; Sophocleous and Atkinson, 2017), and platinum (Daud et al., 2016; Hrapovic et al., 2007; Kim et al., 2024). However, traditional working electrodes present certain challenges, due to lack resilience under harsh conditions, are overly sensitive to dissolved oxygen, and pose difficulties when modification is necessary. To circumvent these limitations, we employ Boron-Doped Diamond (BDD) (Atriardi et al., 2019; Dewandaru et al., 2018; Ivandini et al., 2006; Savitri et al., 2023; Song and Swain, 2007).

BDD is inert, impervious to oxygen, and readily modifiable, making it an ideal choice for working electrodes. Specifically, its surface is modified with platinum to enhance arsenic detection (Bu et al., 2015; Gao et al., 2013; Macpherson, 2015). Drawing inspiration from the work of the Compton group, who investigated arsenic detection using a glassy carbon electrode (GCE) modified with platinum (Toor et al., 2015), we propose a novel approach. By incorporating the unique properties of platinum and BDD, we can fabricate a working electrode that is not only highly efficient but also robust (Bhat et al., 2022; Dewandaru et al., 2018; Song and Swain, 2007).

The modification with platinum amplifies the electrochemical reactivity of the BDD surface, making it a prime candidate for arsenic detection (Dai and Compton, 2006). In this research, we delve into the modification of the BDD electrode through the application of the wet seeding technique and subsequent electrodeposition. We aim to thoroughly examine its redox properties, scrutinize the morphological structure of the deposited platinum, and evaluate its efficacy as an electrochemical arsenic detector in a phosphate buffer. This endeavor is anticipated to shed light on more effective arsenic detection methodologies, thereby enhancing our ability to monitor and mitigate environmental hazards.

## 2. Methods

### 2.1 Apparatus and chemical

Chemicals applied in this study were sodium arsenite ( $\text{NaAsO}_2$ ), sodium arsenate ( $\text{Na}_3\text{AsO}_4$ ), hydrogen hexachloroplatinate (IV) hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), phosphate buffer saline (PBS), sodium borohydrate ( $\text{NaBH}_4$ ), methanol ( $\text{CH}_3\text{OH}$ ) and deionized (DI) water was used in the preparation of chemical solutions. Apparatus also used were boron-doped diamond (BDD), Teflon, silicon, platinum spiral, Ag/AgCl (saturated KCl) reference electrode, fused silica capillary, syringe, magnetic stirrer, stirrer bar, hotplate, sonicator, screw vial, and extension cable.

### 2.2 Pt modified BDD (BDD/Pt)

Modification using wet seeding was performed by dripping  $\text{NaBH}_4$  and  $\text{H}_2\text{PtCl}_6$  on the surface of solution and letting it precipitate for one day, washed using double distilled water, then dried using  $\text{N}_2$  gas; this treatment was repeated three times. Then, electrodeposition was conducted using  $\text{H}_2\text{PtCl}_6$  solution at a potential of  $-0.2$  V for 15 minutes. After that, electrode was calcinated using Rapid Thermal Annealing (RTA) for 5 minutes at  $700^\circ\text{C}$  in free oxygen condition. The modifying result was then characterized with Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) by JEOL JSM-IT200 which later applied as a working electrode for arsenic trace detection.

### 2.3 $\text{As}^{3+}$ and $\text{As}^{5+}$ detection procedure

Application testing employs a BDD/Pt working electrode with a phosphate buffer solution containing various concentrations of  $\text{As}^{3+}$  and  $\text{As}^{5+}$ .  $\text{As}^{3+}$  was detected at a deposition potential of  $-500$  mV for 150 seconds, with a stripping rate of 200 mV/s. For  $\text{As}^{5+}$  detection, 0.1 M  $\text{NaBH}_4$  was inserted and stirred for 1 minute to reduce  $\text{As}^{5+}$  to  $\text{As}^{3+}$ , followed by deposition under the same condition. For detecting a mixture of  $\text{As}^{3+}$  and  $\text{As}^{5+}$ , ASV was initially performed to measure the  $\text{As}^{3+}$  concentration. Subsequently, 0.1 M  $\text{NaBH}_4$  was added and stirred for 1 minute, and ASV was repeated to determine the total arsenic concentration. The  $\text{As}^{5+}$  concentration was then obtained by subtracting the  $\text{As}^{3+}$  concentration from the total arsenic concentration.

## 3. Results and Discussion

### 3.1 Modifying BDD/Pt

Modification of BDD surface combines wet seeding to grow the crystal nuclei of Pt at the BD surface with the following reaction (Equation 1):



Electrodeposition was then conducted to grow the Pt crystal on the BDD surface. Figure 1 shows the SEM characterization result of the BDD/Pt modification process. Figure 1 displays the surface alterations of the BDD when subjected to two distinct modification techniques: wet seeding followed by electrodeposition (BDD/Pt-2), and solely the wet seeding method (BDD/Pt-7).

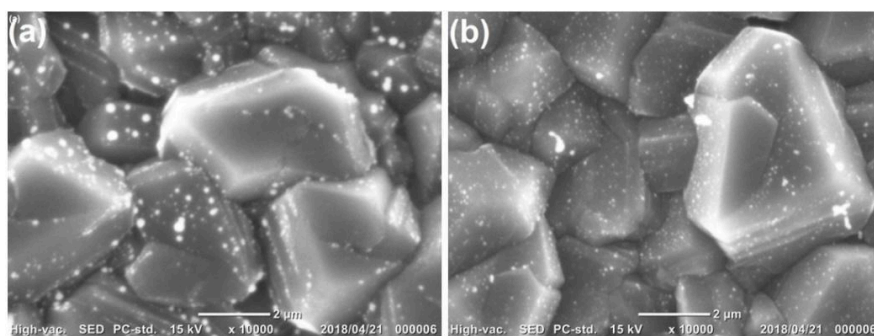


Fig. 1. SEM images of (a) BDD/Pt-2 and (b) BDD/Pt-7 (Bar = 2  $\mu\text{m}$ )

The comparative analysis reveals that the BDD/Pt-2 modification, which incorporates the wet seeding technique, which was succeeded by electrodeposition, engenders a larger Pt size relative to the BDD/Pt-7 modification, which exclusively employs the wet seeding technique. Regardless of the fact that the latter technique, devoid of subsequent electrodeposition, engenders a lower Pt concentration on the BDD surface (0.94%) and a reduced Pt particle size, yielding a significantly lower current response. Moreover, the oxidation peak in the arsenite test is indistinct (as depicted in Figure 1).

Table 1. Comparison of element composition in % mass on the BDD/Pt surface

Element	Wet seeding	Electrodeposition
Carbon	96.74	95.71
Oxygen	2.32	2.74
Platina	0.94	1.54

Consequently, the BDD/Pt-2 variant, characterized by a higher surface Pt concentration (1.54%) and an increased Pt size, elicits a superior current response, and engenders a distinct oxidation peak in the arsenite test. Thus, the variant is suitable to be applied as a working electrode for arsenic detection. Concurrently, Figure 2 and Table 1 present the compositional analysis of the compounds detected on the BDD surface.

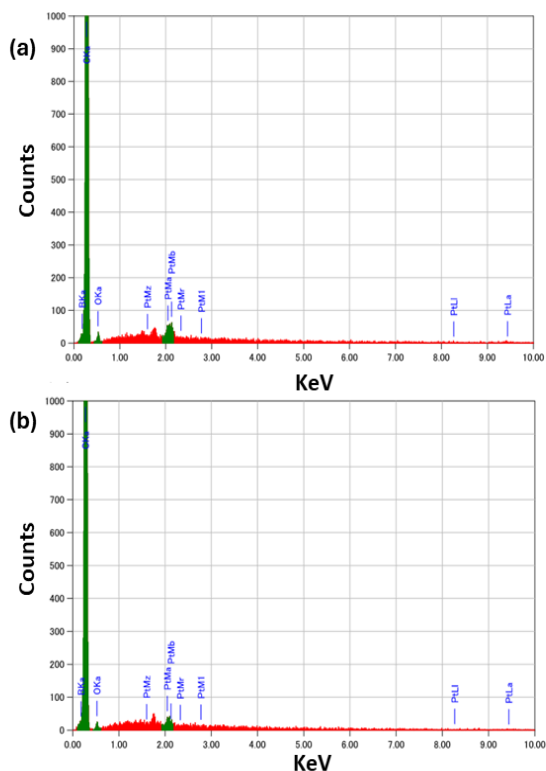


Fig. 2. Elemental composition spectrum on the surface of BDD/Pt-2 and BDD/Pt-7

### 3.2 Determination of optimum $\text{NaBH}_4$ concentration

The process of the reducing agent  $\text{NaBH}_4$  addition facilitates the measurements at low negative potentials. The  $\text{As}^{3+}$  species are easier to measure using the ASV technique because the negative potential used for the deposition process is low, whereas the  $\text{As}^{5+}$  species require a very high negative potential; thus, the  $\text{As}^{5+}$  deposition process using the ASV technique can be disrupted by the formation of hydrogen gas, which competes with the reduction of  $\text{As}^{5+}$  at the same potential, which is very negative. This disturbance during  $\text{As}^{5+}$  deposition can be reduced by pretreatment with the addition of the  $\text{NaBH}_4$  reducing agent. The  $\text{As}^{5+}$  species added with  $\text{NaBH}_4$  are reduced to  $\text{As}^{3+}$ , enabling the deposition process to proceed under low negative potential.

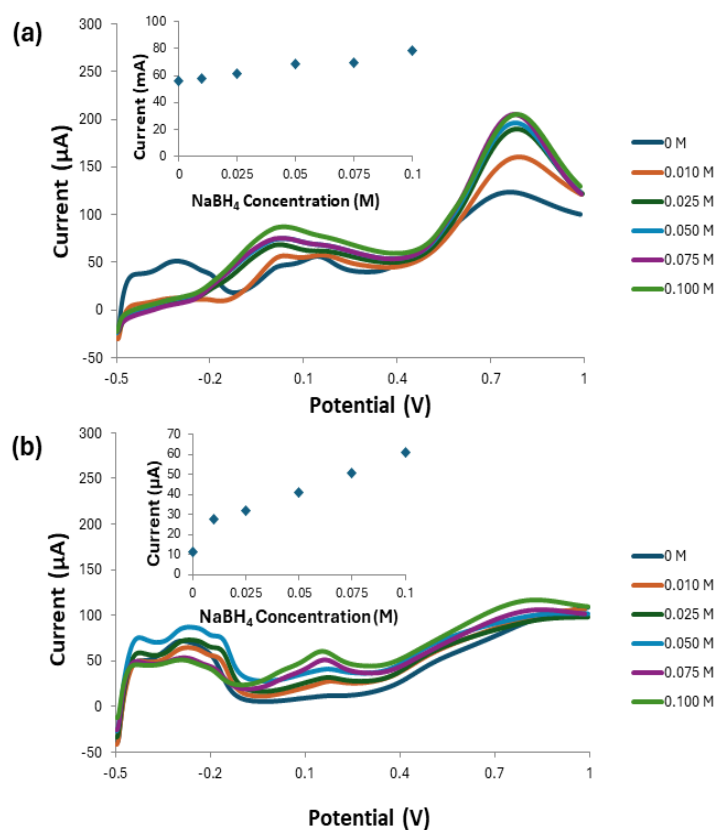


Fig. 3. Species reduction voltammogram along with current response plot for (a)  $\text{As}^{3+}$  and (b)  $\text{As}^{5+}$  with varying concentrations of  $\text{NaBH}_4$

The measurements were performed without deposition at a detection rate of 100 mV/s. The results display the voltammogram results of the addition of varied  $\text{NaBH}_4$  concentration at 2.5 ppm  $\text{As}^{3+}$  and  $\text{As}^{5+}$  in PBS at pH 6 (Figure 3). It can be seen that the oxidation peak of  $\text{As}^0$  to  $\text{As}^{3+}$  is observed at a potential around 0.15 V, but in the voltammogram of the  $\text{As}^{3+}$  species (Figure 3a), three oxidation peaks appear at around 0.03, 0.15, and 0.8 V. The oxidation peaks at potentials 0.03 and 0.15 V are the result of the oxidation of  $\text{As}^0$  to  $\text{As}^{3+}$ , and the presence of these two oxidation peaks indicates that the arsenic formed on the surface of the working electrode forms a double layer. Furthermore, a potential of 0.03 V indicates the oxidation of  $\text{As}^0$  on the double layer, which is oxidized to  $\text{As}^{3+}$ , while a potential of 0.15 V indicates the oxidation of the  $\text{As}^0$  layer on the surface, which is oxidized to  $\text{As}^{3+}$ . The increase in the oxidation peak at a potential of 0.03 V indicates that the Pt surface was completely covered by reduced  $\text{As}^0$ , whereas the remaining as in the solution was reduced to  $\text{As}^0$ , creating a double layer. The oxidation peak at a potential of 0.8 V is the result of the oxidation process of  $\text{As}^{3+}$  to  $\text{As}^{5+}$ .

Simultaneously in Figure 3b, the oxidation peak produced from the arsenate solution is not significantly different from that of the arsenite solution. However, there is a fundamental difference, namely that the oxidation peak produced at a potential of 0.15 V is higher than that at 0.03 V because the arsenic double layer is not formed on the Pt surface due to the small arsenate concentration used. From the conducted tests, it can be concluded that the optimal concentration for adding  $\text{NaBH}_4$  is 0.1 M.

### 3.3 Determination of optimum deposition potential

The determination of the optimum deposition potential was carried out at potential variations of -100, -200, -300, -400, and -500 mV with a deposition time of 150 s and a detection rate of 100 mV/s. The deposition potential is the potential used to reduce as from solution to  $\text{As}^0$  such that it forms a layer on the surface of the working electrode. The determination of the optimal deposition potential will be carried out using a 2.5 ppm arsenite solution with and without the addition of  $\text{NaBH}_4$  solution and a 2.5 ppm arsenate solution with the addition of  $\text{NaBH}_4$  solution. The results of the ASV voltammograms of the arsenite and arsenate solutions can be seen in Figure 4a and 4b.

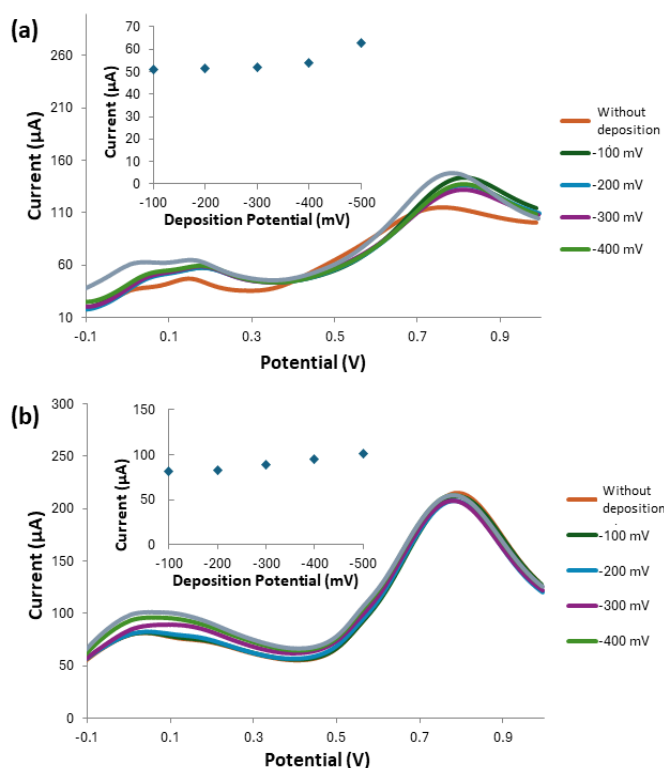


Fig. 4. Stripping voltammogram and current response plot of 2.5 ppm  $\text{As}^{3+}$  (a) and  $\text{As}^{5+}$  (b) with respect to variations in deposition potential

In a 2.5 ppm arsenite solution, the deposition potential was determined without and with the addition of  $\text{NaBH}_4$ . This was done to determine the change of  $\text{As}^0$  oxidation peak to  $\text{As}^{3+}$  during the two processes. Arsenite deposited with the addition of  $\text{NaBH}_4$  has a higher current response at a potential of around 0.03 V or 0.15 V. With the addition of  $\text{NaBH}_4$ , it can be seen that the oxidation peak at 0.03 V is higher than 0.15 V, this indicates that the surface of the working electrode used is covered by a layer so that the arsenic remaining in the solution is reduced to form other layers that bind to the arsenic on the surface. In the detection of arsenite without the addition of  $\text{NaBH}_4$ , the arsenic oxidation peak is still clearly visible at 0.15 V. Because arsenite can be easily reduced without the addition of  $\text{NaBH}_4$ , the ASV process for the arsenite solution will not use the addition of  $\text{NaBH}_4$ .

Figure 4 shows that a more negative deposition potential provides a greater response current for the oxidation of  $\text{As}^0$  to  $\text{As}^{3+}$  at a potential of around 0.15 V. This occurs because a large amount of  $\text{As}^0$  is formed during deposition, which reduces  $\text{As}^{3+}$  to  $\text{As}^0$ . A low deposition potential will prevent the bonds breakage in arsenite so that the arsenite is not reduced; however, a potential that is more negative than -500 mV will cause the formation of  $\text{H}_2$  gas, which will disrupt the background current so that it becomes too large and causes the arsenic oxidation peak to become invisible (Zhang et al., 2022). Therefore, the deposition potential of the ASV process in arsenite solution was determined to be -500 mV. Arsenate has a stronger bond than arsenite, and thus, requires more negative potential to be reduced (Chen et al., 2016). This can interfere with detection because a very negative potential triggers the formation of  $\text{H}_2$  such that the process of arsenic deposition onto the surface competes with the formation of  $\text{H}_2$ . Therefore, adding  $\text{NaBH}_4$  to arsenic solutions can help to reduce arsenic.

### 3.4 Determination of optimum deposition time

The determination of the optimal deposition time to reduce  $\text{As}^{3+}$  to  $\text{As}^0$  was carried out at time variation of 30, 60, 90, 120, 150, 180, and 210 s with an optimal deposition potential of -500 mV and a detection rate of 100 mV/s. Figure 5a and 5b show the stripping voltammograms of 2.5 ppm  $\text{As}^{3+}$  and  $\text{As}^{5+}$  species on a Pt electrode as a reference for testing using a BDD/Pt working electrode.

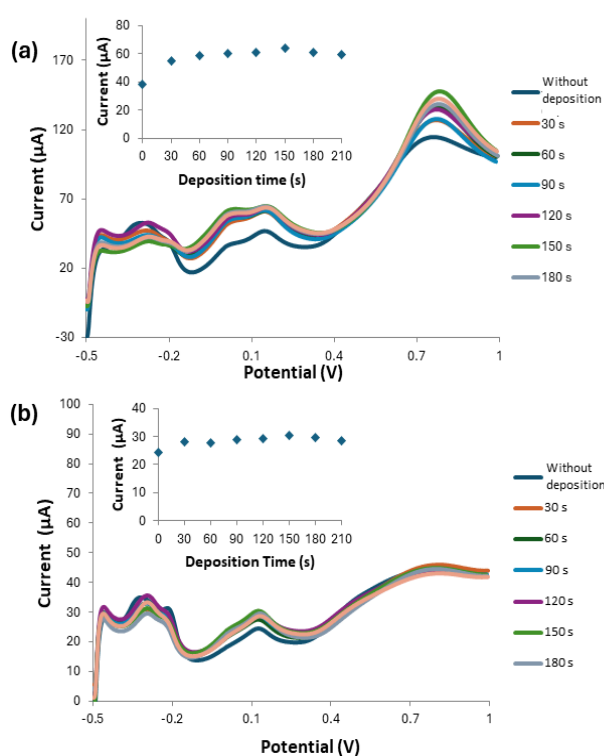


Fig. 5. Stripping voltammogram and current response plot of 2.5 ppm  $\text{As}^{3+}$  (a) and  $\text{As}^{5+}$  (b) with respect to variations in deposition time

The deposition time to reduce  $\text{As}^{5+}$  to  $\text{As}^0$  assisted by the addition of  $\text{NaBH}_4$  or  $\text{As}^{3+}$  to  $\text{As}^0$  at a deposition time of 150 s gave a higher oxidation peak, but deposition times greater than 150 s experienced a decrease in the oxidation peak. This extra time was due to a decrease in the oxidation current produced during stripping, which caused the arsenic in the solution to be completely reduced and bound to form a layer on the working electrode. Thus, excess time also reduced the number of other compounds, resulting in the formation of a new layer. This caused the oxidation current detected during stripping to become higher and unstable.



### 3.5 Determination of optimum detection rate

The detection rate is a variable used to regulate the diffusion layer in the testing process (Krejci et al., 2014). A high detection rate allows the diffusion layer to become thinner, facilitating electron transfer on the electrode surface and producing high current. On the other hand, at a low detection rate, the diffusion layer becomes thick, and the electron transfer process on the electrode surface becomes slow, reducing the current. Determining the detection rate also needs to be optimal because a detection rate that is too fast can also cause oxidation or reduction peaks at adjacent potentials to be detected as just one peak (Levine et al., 2014).

Determination of the optimal detection rate of  $\text{As}^{3+}$  and  $\text{As}^{5+}$  were conducted at various detection rates of 100, 200, 320, 400, and 500 mV/s with a deposition potential of -500 mV and a deposition time of 150 s. As shown in Figure 6, it can be seen that the faster detection rate results in the oxidation peak in the process of stripping  $\text{As}^0$  to  $\text{As}^{3+}$  becoming larger and shifting toward a more positive potential. This indicates that the oxidation of  $\text{As}^0$  to  $\text{As}^{3+}$  requires a more positive potential. Furthermore, the increase in the oxidation current response does not interfere with arsenic detection because the oxidation peak can still be seen clearly and the current peak from variations in this detection rate gives a linear response of 0.9995 for the arsenite solution and 0.9932 for the arsenate solution.

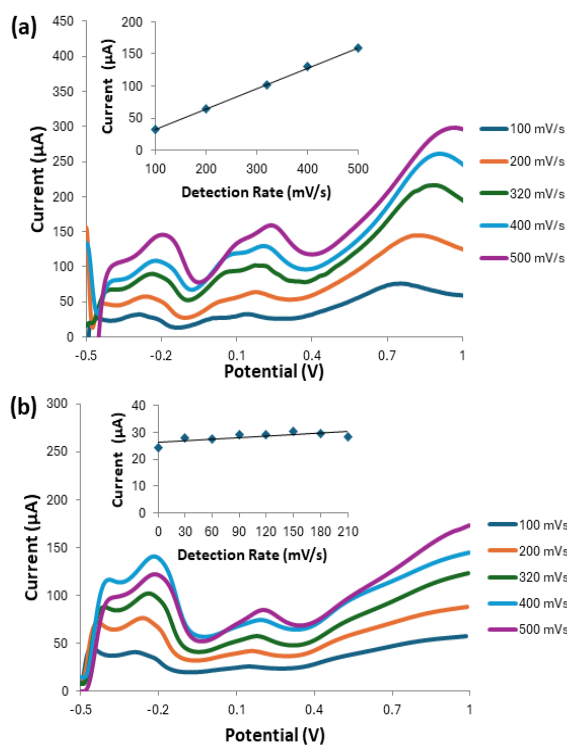


Fig. 6. Stripping voltammogram and current response plot of 2.5 ppm  $\text{As}^{3+}$  (a) and  $\text{As}^{5+}$  (b) with respect to variations in detection rate

The detection rate that will be employed for the subsequent test is not the fastest, even if it offers a linear response to arsenic detection. This is due to the fact that excessively fast detection rates reduce the amount of interaction between the analyte and the electrode surface, but excessively slow detection rates may result in additional reactions on the electrode surface during the stripping procedure. Thus, 200 mV/s will be the detection rate that is utilized as the ideal detection rate (Stuckey, 2011).



### 3.6 As<sup>3+</sup> detection

The sensitivity of arsenic detection using BDD/Pt towards As<sup>3+</sup> is done with concentration variations of 0–1000 ppb, as revealed in Figure 7. In the ASV process, PBS containing As<sup>3+</sup> was deposited at a potential of -500 mV, deposition time of 150 s, and stripping rate of 200 mV/s. The deposition process during ASV was conducted to determine the preconcentration of As<sup>3+</sup> in the solution and to reduce As<sup>3+</sup> to As<sup>0</sup> on the surface of the working electrode. Subsequently, the stripping process results in an oxidation peak, where As<sup>0</sup> is converted back into As<sup>3+</sup> in the solution. As shown in Figure 7(a), two peaks appear at 0.03 V (A) and 0.15 V (B). The oxidation peak for the conversion of As<sup>0</sup> to As<sup>3+</sup> is represented by point (B), while point (A) corresponds to the oxidation peak for double-layer arsenic. This double layer forms when the arsenic concentration in the solution is significantly high and no more Pt sites are available for arsenic interaction.

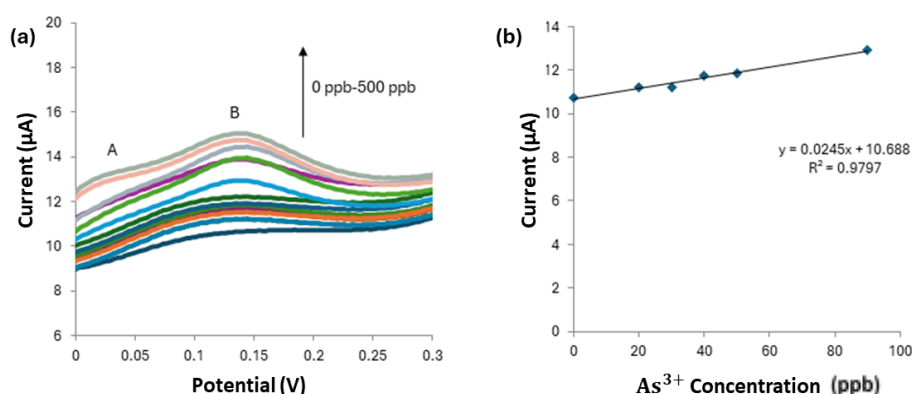


Fig. 7. (a) Stripping voltammogram of various concentrations of As<sup>3+</sup>, (b) Plot I vs As<sup>3+</sup> concentration. Stripping voltammetry parameters were  $E_{\text{dep}} = -0.5$  V,  $t_{\text{dep}} = 150$  s and scan rate = 200 mV/s

### 3.7 As<sup>5+</sup> detection

The As<sup>5+</sup> detection with BDD/Pt at concentrations of 0–1000 ppb, as displayed in Figure 8. In the detection of As<sup>5+</sup>, NaBH<sub>4</sub> addition as reductor is required because As<sup>5+</sup> needs a very negative potential to be reduced on the surface of BDD/Pt, which can cause a reduction competition between As<sup>5+</sup> and hydrogen evolution, rendering the reduction As<sup>5+</sup> on the surface of BDD/Pt imperfect. Following the NaBH<sub>4</sub> addition, the solution was stirred for 1 min before ASV. Figure 8a shows that at a potential of 0.03 V (A), almost no double-layer arsenic was detected. This occurred because the arsenic concentration on the BDD/Pt surface was low enough that the arsenic is fully reduced on the BDD/Pt surface. A plot of the current response vs. As<sup>5+</sup> detection is shown in Figure 8b.

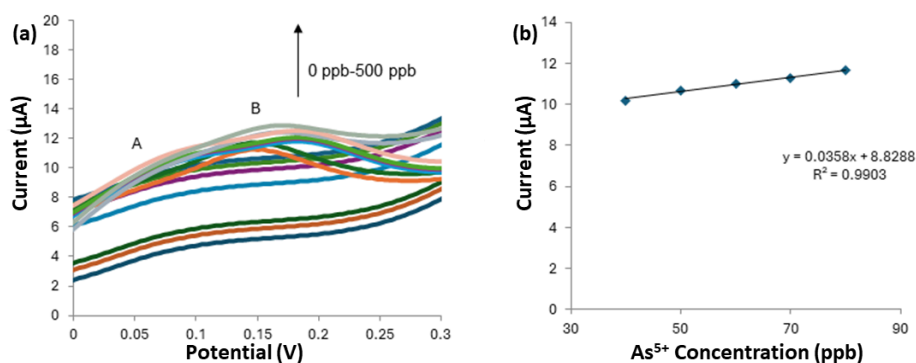


Fig. 8. (a) Stripping voltammogram of various concentrations of As<sup>5+</sup>, (b) Plot I vs As<sup>5+</sup> concentration. Stripping voltammetry parameters were  $E_{\text{dep}} = -0.5$  V,  $t_{\text{dep}} = 150$  s and scan rate = 200 mV/s

### 3.8 $As^{3+}$ and $As^{5+}$ mixture detection

Detection in a mixture was performed twice with ASV, in which the first ASV treatment was conducted for  $As^{3+}$  determination, with addition of  $NaBH_4$  and stirring for 1 min. The second ASV treatment is done for total arsenic concentration determination, where  $As^{5+}$  can be calculated from subtraction of  $As^{3+}$  from the total arsenic concentration. Two batches of tests were performed. In the first batch, 100 ppb sodium arsenite was applied as the constant variable with an additional variable of 100–400 ppb sodium arsenite. In the second batch, sodium arsenate was applied as the constant variable and 100–400 ppb sodium arsenite was used as an additional variable, as shown in Figure 9. No double-layered arsenic was formed.

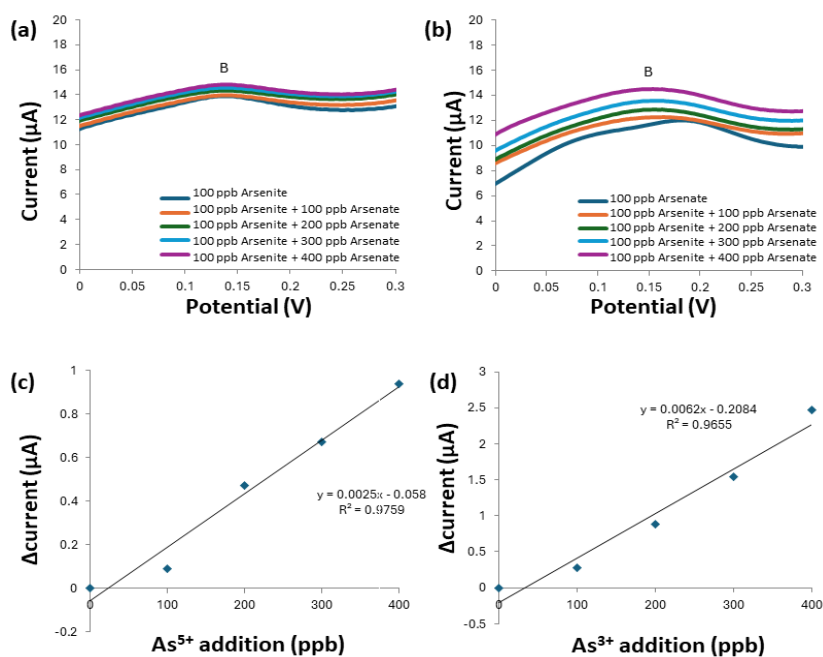


Fig. 9. Stripping voltammogram of 100 ppb (a)  $As^{3+}$  and various concentration of  $As^{5+}$ , (b)  $As^{5+}$  and various concentration of  $As^{3+}$ , (c) Plot I vs various concentration of  $As^{5+}$  addition and (d) Plot I vs various concentration of  $As^{3+}$  addition. Stripping voltammetry parameters were  $E_{dep} = -0.5$  V,  $t_{dep} = 150$  s and scan rate = 200 mV/s

Figure 9c shows that  $As^{3+}$  and  $As^{5+}$  can be tested simultaneously, as can be seen with a linearity of 0.9759 for 100 ppb sodium arsenite and an additional variation of sodium arsenate. In Figure 9d, the detection of 100 ppb sodium arsenate and the addition variation of sodium arsenite have a linearity of 0.9655.

### 3.9 Electrode stability

The stability of BDD/Pt was tested to determine the time and extent of Pt particle stability on the BDD surface during the detection of  $As^{3+}$  and  $As^{5+}$  in an interval of five days under optimal conditions using ASV. The percentage RSD obtained was less than 3%, therefore it is concluded that the BDD/Pt electrode is sufficiently stable for prolonged use to detect both  $As^{3+}$  and  $As^{5+}$  species. The Figure 10 plots the current response versus electrode stability for the BDD/Pt electrode.

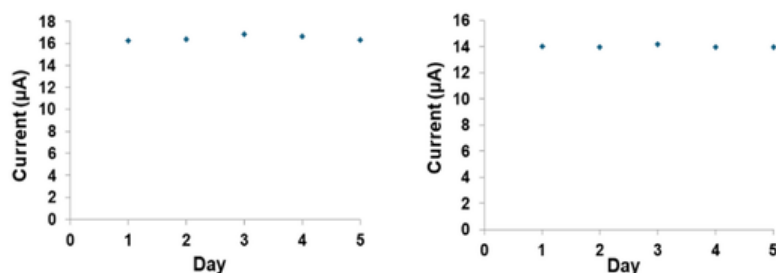


Fig. 10. Plot I vs detection day of (a)  $\text{As}^{3+}$  and (b)  $\text{As}^{5+}$ . Stripping voltammogram of 100 ppb (a)  $\text{As}^{3+}$  and various concentration of  $\text{As}^{5+}$ , (b)  $\text{As}^{5+}$  and various concentration of  $\text{As}^{3+}$ , Stripping voltammetry parameters were  $E_{\text{dep}} = -0.5 \text{ V}$ ,  $t_{\text{dep}} = 150 \text{ s}$  and scan rate =  $200 \text{ mV/s}$

#### 4. Conclusions

This study has successfully modified boron-doped diamond (BDD) electrodes with platinum (Pt) via a wet seeding process followed by electrodeposition, achieving a uniform Pt coverage of 1.54%, as confirmed by SEM-EDS analysis. The modified BDD/Pt electrodes demonstrated the capability to simultaneously detect  $\text{As}^{3+}$  and  $\text{As}^{5+}$  using anodic stripping voltammetry (ASV). Optimal conditions for  $\text{As}^{5+}$  detection were established by initially adding 0.1 M  $\text{NaBH}_4$  to reduce  $\text{As}^{5+}$  to  $\text{As}^{3+}$ , followed by detection at a potential of  $-500 \text{ mV}$  for 90 s with a scan rate of  $200 \text{ mV/s}$ . Under these conditions, ASV measurements with BDD/Pt electrodes exhibited high linearity over a concentration range of 0 to 100 ppb, with correlation coefficients of 0.9797 for  $\text{As}^{3+}$  and 0.9903 for  $\text{As}^{5+}$ . The tests demonstrated good precision and stability, with a relative standard deviation (RSD) below 3%. These findings indicate that the modified BDD/Pt electrodes are highly effective and reliable for arsenic detection and speciation analysis, highlighting their potential for environmental monitoring applications.

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Conceptualization, F.R.A.A.F., R.S.; Validation, H.M., R.K.P., A.S.; Formal Analysis, F.R.A.A.F., R.S., A.S., H.M., R.K.P.; Data Curation, F.R.A.A.F., R.S., A.S.; Writing – Original Draft Preparation, F.R.A.A.F., R.S.; Writing – Review & Editing, H.M., R.K.P.; Supervision, A.S., R.K.P.; and Funding Acquisition, A.S., R.K.P.

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#### Ethical Review Board Statement

Not applicable.

## Informed Consent Statement

Informed consent was obtained from all subjects involved in the study.

## Data Availability Statement

Not available.

## Conflicts of Interest

The authors declare no conflict of interest.

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