

Research Article

Anodic Stripping Voltammetry of Se^{4+} on Gold-Modified Boron-Doped Diamond Electrodes

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Electrochemical detection of Se^{4+} has been performed by anodic stripping voltammetry on a boron-doped diamond (BDD) electrode modified with gold nanoparticles deposited through chronocoulometry. This method is based on the affinity between the gold nanoparticles and Se^0 , while the BDD electrode is presented as an ideal material for metal modification due to its unique properties. The resulting anodic stripping voltammograms exhibited a clear peak at 0.9 V versus AgCl related to Se^{4+} , and highly accurate ($r^2 = 0.99$) calibration curves could be obtained for a selenium concentration range between 10 and 100 $\mu\text{g/L}$. The influence of Se deposition time and other metals dissolved in solution (Cu, Cd, Pb, Cr, and B) has been investigated as well, and it was found that the Se^{4+} calibration curves remained unaltered. For all the experiments performed, a detection limit around 10 $\mu\text{g/L}$ was achieved. The high accuracy and reproducibility of the results as well as the excellent stability of the electrode material proves the excellent capabilities of this system for selenium detection.

1. Introduction

Selenium is an essential micronutrient for animals and humans but can be extremely toxic if absorbed in large doses (over 400 μg per day) [1]. Exceeding the tolerable upper intake level of 400 micrograms per day (15 μg per kg bodyweight) can lead to selenosis, which affects the respiratory, digestive, and neurological systems [2]. The maximum contaminant level of selenium in water allowed by the US Environmental Protection Agency is 50 $\mu\text{g/L}$ [3].

Selenium exists in many forms in the environment, but the most abundant are H_2SeO_3 (Se^{4+}), H_2SeO_4 (Se^{6+}), and their derivatives [4]. The quantification of both forms is important because Se species vary in their toxicity potential to animals and humans. However, if one sample contains both Se^{4+} and Se^{6+} species, it is possible to reduce the Se^{6+} to Se^{4+} by heating the sample at 85°C in concentrated HCl [4]. The concentration of Se in this solution is then considered as the sum of Se^{4+} and Se^{6+} . The difference between

the concentration of Se in digested and undigested samples is the concentration of Se^{6+} . Many techniques have been developed in order to analyze Se^{4+} concentrations at the $\mu\text{g/L}$ level but the most common method is stripping voltammetry due to its simplicity, rapidity, and excellent sensitivity. Both cathodic stripping voltammetry using a hanging mercury drop electrode [5–11] and anodic stripping voltammetry (ASV) using gold (rotating disk or film) electrodes [12–14] have been extensively studied for Se^{4+} determination in acidic solutions. These methods have been shown to be quite efficient for selenium determination. However, the anodic stripping on gold electrodes usually requires time-consuming pretreatments of the gold electrode in order to get reproducible results. Moreover, the main problem of these methods is the splitting of the stripping peaks [5, 6]. Several methods have been proposed to solve this problem like increasing the temperature of the support electrolyte [6, 8] or adding small amounts of copper or rhodium to the solutions [7–9, 11, 15]. Nevertheless, these steps tend

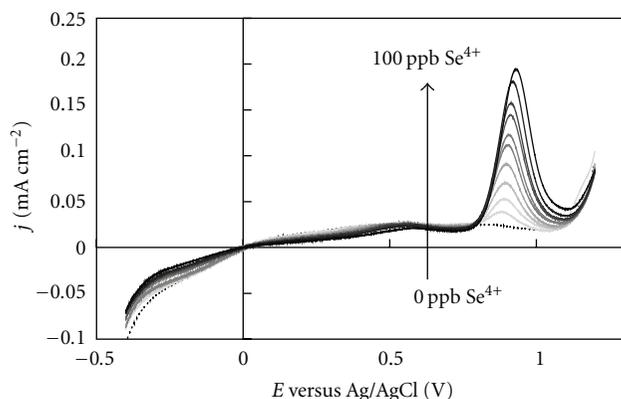


FIGURE 1: Stripping voltammograms of Se^{4+} in 0.1 M HClO_4 in the concentration range of 0–100 $\mu\text{g/L}$ recorded on a BDD electrode, which was previously modified by gold nanoparticles deposited by chronocoulometry (-35 mC cm^{-2} was applied for 1 minute in a solution of HAuCl_4 100 ppm in 0.1 M HCl). The deposition potential (-0.4 V versus Ag/AgCl) was applied during 2 minutes before the stripping, which was performed at a scan rate of 200 mV/s . The upper potential limit was fixed at 1.2 V versus Ag/AgCl . $T = 23^\circ\text{C}$.

to complicate the experimental procedure, and added to the delicate handling of mercury electrodes, these methods become less suited for real analytical applications.

In this work, the detection of Se^{4+} by anodic stripping voltammetry on gold-modified boron-doped diamond electrode is presented for the first time. BDD has been selected for gold deposition due to its outstanding properties compared to other conventional electrode materials such as a wide electrochemical potential window, low background current, and weak adsorption of polar molecules [16, 17]. These properties offer a significant advantage for metal modification as it was already shown for the detection of As^{3+} and As^{5+} mixtures [18]. Moreover, the high stability of these gold-modified BDD electrodes has been shown [18]. Therefore, the same method has been used for selenium detection in this study. Concentration of Se^{4+} was measured by a stripping method based on the simple electrochemical reduction of Se^{4+} to Se^0 followed by oxidation of the latter. The influence of Se deposition time is discussed. Moreover, the selective detection of Se^{4+} in the presence of interference metal ions was also studied.

2. Experimental

2.1. Chemicals and Materials. Selenious acid (H_2SeO_3), hydrogen tetrachloroaurate(III) trihydrate (HAuCl_4), hydrogen chloride (HCl), perchloric acid (HClO_4), copper chloride (CuCl_2), lead chloride (PbCl_2), boric acid (H_3BO_3), cadmium chloride (CdCl_2), and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were purchased from Wako. All chemicals were used without further purification.

2.2. Preparation of BDD Electrodes. BDD thin films were deposited using a microwave plasma-assisted chemical vapor deposition (MPCVD) setup (ASTeX Corp.). Acetone was

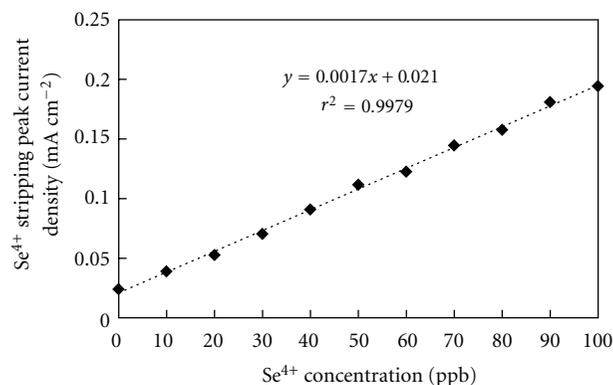


FIGURE 2: Calibration curve from the anodic stripping voltammograms presented in Figure 1. The peak current was plotted as a function of Se^{4+} concentration.

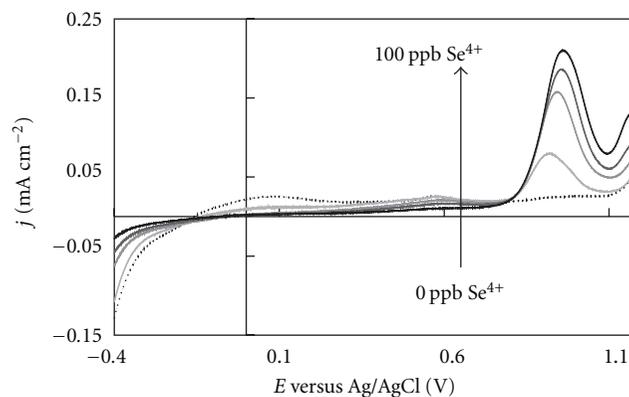


FIGURE 3: Stripping voltammograms of Se^{4+} in 0.1 M HClO_4 in the concentration range of 0–100 $\mu\text{g/L}$ recorded on a BDD electrode, which was previously modified by gold nanoparticles deposited by chronocoulometry (-70 mC cm^{-2} was applied for 1 minute in a solution of HAuCl_4 100 ppm in 0.1 M HCl). The deposition potential (-0.4 V versus Ag/AgCl) was applied during 2 minutes before the stripping, which was performed at a scan rate of 200 mV/s . The upper potential limit was fixed at 1.2 V versus Ag/AgCl . $T = 23^\circ\text{C}$.

used as carbon source and $\text{B}(\text{OCH}_3)_3$ as boron source. The concentration of the latter was 0.1% w/w in source. The surface morphology and crystalline structures were characterized using scanning electron microscopy (not shown in this work). The typical size of the diamond crystals was about $5 \mu\text{m}$. BDD films were deposited on Si (1 0 0) wafers in the MPCVD chamber at 5 kW using high-purity hydrogen as carrier gas. The BDD film thickness was about $40 \mu\text{m}$ after 10 hours of deposition. The Raman spectrum of this film exhibited a sharp peak at 1334 cm^{-1} , which is characteristic of crystalline diamond. The BDD electrodes were pretreated by ultrasonication in 2-propanol for about 10 minutes followed by rinsing with high-purity water in order to remove any organic impurities that may have remained within the BDD film after deposition in the MPCVD chamber.

Gold-modified BDD electrodes were prepared through the same procedure reported in [19]. The BDD electrode

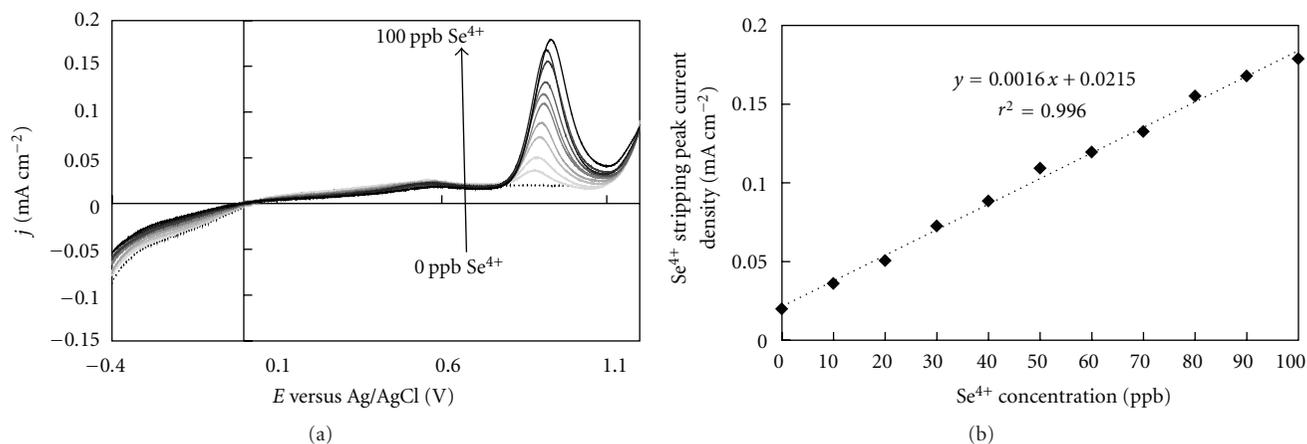


FIGURE 4: (a) Stripping voltammograms of Se^{4+} in 0.1 M HClO_4 in the concentration range of 0–100 $\mu\text{g/L}$ recorded on a BDD electrode, which was previously modified by gold nanoparticles deposited by chronocoulometry (-35 mC cm^{-2} was applied for 1 minute in a solution of HAuCl_4 100 ppm in 0.1 M HCl). The deposition potential (-0.4 V versus Ag/AgCl) was applied for 1 minute before the stripping, which was performed at a scan rate of 200 mV/s . The upper potential limit was fixed at 1.2 V versus Ag/AgCl . (b) Calibration curve extracted from these stripping voltammograms. $T = 23^\circ\text{C}$.

was immersed in 0.1 M HCl solution containing 100 ppm of HAuCl_4 , and gold nanoparticles deposition was performed through chronocoulometry.

2.3. Electrochemical Measurements. Electrochemical measurements were carried out in a single-compartment cell using a Hokuto Denko Hz-5000 potentiostat at room temperature (23°C). The reference electrode was Ag/AgCl , the counter electrode was a platinum wire, and the working electrode was BDD. The working geometric area was 0.283 cm^2 . The anodic stripping of Se was performed in 0.1 M HClO_4 , whereas the posttreatment was carried out in 0.1 M HCl . In this work, all potentials given are with respect to the Ag/AgCl reference electrode (0.2 V versus SHE).

3. Results and Discussion

3.1. Anodic Stripping Voltammetry of Se^{4+} . The anodic stripping voltammetry of Se^{4+} has been performed based on its reduction to Se^0 followed by oxidation of the latter. For the first measurements, gold particles were deposited through chronocoulometry at -35 mC cm^{-2} for 1 minute. A deposition potential of -0.4 V has been applied during 2 minutes for Se deposition because the Se^{4+} reduction peak was observed around that potential on gold-modified BDD electrodes (result not shown). For the stripping of selenium, the voltammetric scan was performed between the deposition potential (-0.4 V) and different upper limit potentials. The resulting voltammograms related to solutions containing different concentrations of Se^{4+} (from 10 to 100 $\mu\text{g/L}$ dissolved in 0.1 M HClO_4) are displayed in Figure 1 for upper limit potential of 1.2 V . When the upper limit potential was fixed at 1.4 V , almost the same voltammogram as Figure 1 was observed (not shown). Both figures show the presence of a clear stripping peak situated at 0.9 V approximately, which is related to selenium. Therefore, an upper potential limit

of 1.2 V was selected for the anodic stripping voltammetry measurements. The peak currents obtained from Figure 1 were therefore plotted as a function of Se^{4+} concentration, and the resulting graph (presented in Figure 2) shows that a linear and highly accurate calibration curve ($r^2 = 0.99$) could be obtained under these conditions for a Se^{4+} concentration range between 10 and 100 $\mu\text{g/L}$.

One set of measurements was performed on a gold-modified electrode where the chronocoulometry was performed at -70 mC cm^{-2} for 1 minute, and the resulting anodic stripping voltammograms presented on Figure 3 exhibit a similar profile; therefore, the charge applied during the modification of the BDD electrode was fixed at -35 mC cm^{-2} .

The influence of selenium deposition time was also studied. In fact, it was reduced from 2 to 1 minute. The resulting voltammograms together with the corresponding calibration curve are displayed on Figures 4(a) and 4(b), respectively. These results show that the time during which the deposition potential is applied has no influence neither on the profile of the stripping voltammograms nor on the accuracy of the corresponding calibration curve.

3.2. Influence of Other Metal Ions. In order to evaluate the influence of other metal ions present in the media, a mixture containing cadmium, copper, boron, chromium, and lead (all at a concentration of 100 $\mu\text{g/L}$) was prepared. Anodic stripping voltammetry measurements were carried out using the aforementioned mixture and under the same conditions as those presented on Figure 1, that is, the BDD electrode was modified through chronocoulometry at -35 mC cm^{-2} for 1 min in a solution of HAuCl_4 100 mg/L in 0.1 M HCl . The deposition potential (-0.4 V) was applied during 2 minutes before performing the stripping voltammetry at 200 mV s^{-1} between -0.4 and 1.2 V . The corresponding anodic stripping voltammograms are presented in Figure 5(a). This figure

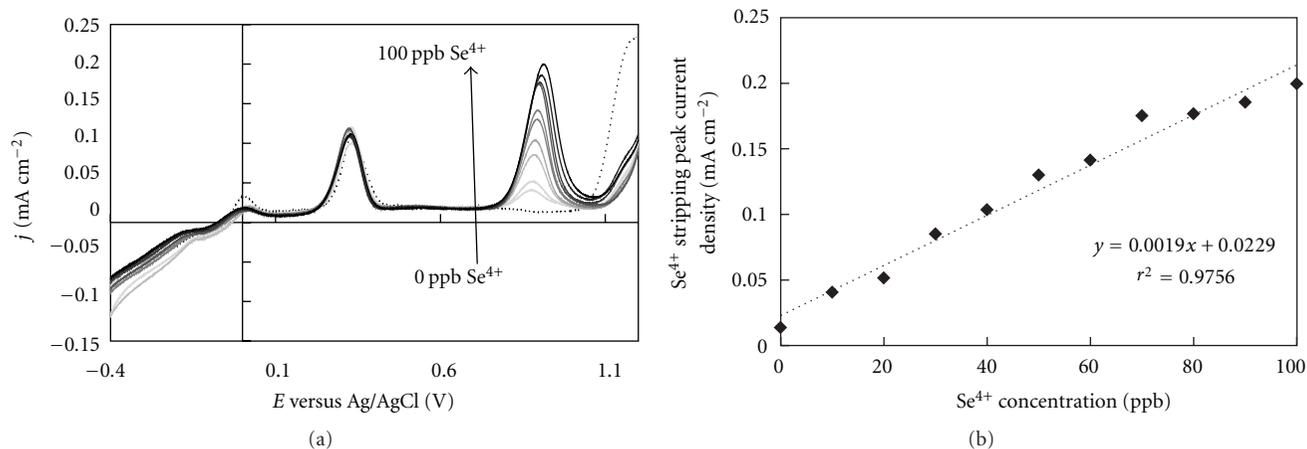


FIGURE 5: (a) Stripping voltammograms of Se^{4+} (concentration range 0–100 $\mu\text{g/L}$) in CuCl_2 , PbCl_2 , H_3BO_3 , CdCl_2 , and $\text{K}_2\text{Cr}_2\text{O}_7$, all 100 $\mu\text{g/L}$ in 0.1 M HClO_4 recorded on a BDD electrode, which was previously modified by gold nanoparticles deposited by chronocoulometry (-35 mC cm^{-2} was applied for 1 minute in a solution of HAuCl_4 100 ppm in 0.1 M HCl). The deposition potential (-0.4 V versus Ag/AgCl) was applied for 2 minutes before the stripping, which was performed at a scan rate of 200 mV/s. The upper potential limit was fixed at 1.2 V versus Ag/AgCl . (b) Calibration curve extracted from these stripping voltammograms. $T = 23^\circ\text{C}$.

shows a clear peak at 0.9 V corresponding to selenium stripping and another peak at 0.3 V which was attributed to the stripping of copper based on measurements performed with each of the interfering metals individually (results not shown). The peaks corresponding to the stripping of the other metals (Cr, Cd, B, and Pb) have a low intensity and are located between 0.2 and 0 V. Nevertheless, Figure 5(a) shows clearly that selenium has the highest affinity with the gold-modified BDD electrode because the intensity of the corresponding stripping peak is the highest when concentration of the interfering metals (100 $\mu\text{g/L}$) is equal to the concentration of selenium.

The intensity of the anodic stripping peak of selenium was then plotted as a function of its concentration. The result, presented in Figure 5(b), shows clearly that the selenium calibration curve is still linear and accurate ($r^2 = 0.97$) despite the presence of many other interfering metals in solution.

4. Conclusions

In this study, the determination of Se^{4+} has been performed through anodic stripping voltammetry on boron-doped diamond electrode modified by gold particles deposited by chronocoulometry. The results have shown that a clear peak related to selenium stripping can be observed at 0.9 V and that highly accurate concentration curve could be constructed for a selenium concentration range between 10 and 100 $\mu\text{g/L}$. The influences of selenium deposition time and gold particles deposition conditions were investigated, and it was found that the accuracy of the calibration curve remained unaltered. The influence of other metal ions in solution was also studied, and the results have shown that selenium has the highest affinity with the type of electrode used herein, and accurate calibration curves for Se^{4+} detection could still be constructed under these conditions.

These results prove that the BDD electrode modified by gold particles is an efficient material for Se^{4+} determination.

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