

## **Boron-doped diamond as the new electrode material for determination of heavy metals**

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### **Abstract**

Nowadays, the new material – boron-doped diamond represents the perspective electrode material which exhibits wide potential range, lower noise and residual current and can be applied in the various solvents, with good resistance to passivation and high chemical stability. The important part of this paper was the study of Zn(II)/Zn redox system using cyclic voltammetry and optimizing of stripping analysis parameters (deposition potential and time). The low limit of detection ( $3 \times 10^{-9}$  mol L<sup>-1</sup>) and quantification ( $1 \times 10^{-8}$  mol L<sup>-1</sup>) indicate that differential pulse anodic stripping voltammetry is a highly sensitive electrochemical method suitable for samples with trace amounts of Zn and other heavy metals. This work also builds on the current trend in the development of new electrode materials and electrochemical study of the environmental samples.

**Keywords:** heavy metal, boron-doped diamond, cyclic voltammetry, stripping analysis

### **Introduction**

There is an increasing demand for sensors able to give a stable response, in short time, but in the same time sensitive, selective, with high precision to use and inexpensive. This necessity led to the development of a new type of electrochemical electrodes, namely, boron-doped diamond (BDD), which have been successfully used in various applications, from biomedical analysis, industrial process analysis to the environmental analysis, especially of heavy metals. Monitoring trace heavy metals like zinc in industrial wastewater is important for human health and the environment (Broadley *et al.*, 2007). The galvanic and battery production industries have the highest zinc emission. Both anthropogenic and natural factors, such as

erosion of sediments and volcanic eruptions, contribute to zinc contamination. Therefore its analytical detection in environment is necessary. Well-established methods for zinc detection are atomic absorption spectroscopy (Madejczyk, Baralkiewicz, 2008; Galgano *et al.*, 2008) and inductively coupled-plasma mass spectrometry (Halicz *et al.*, 2006). Although these methods are highly sensitive, they require expensive and technically demanding equipment. Since most applications do not require such a high sensitivity, a smart alternative is detection with anodic stripping voltammetry (Jones *et al.*, 2007). Anodic stripping analysis has been proved a powerful and versatile technique for the determination of trace amounts of zinc in various samples.

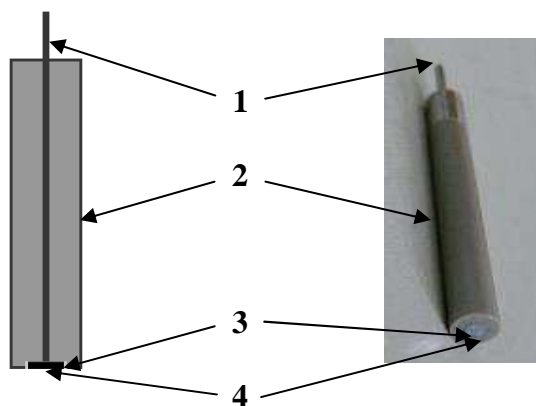
The determination of zinc and other heavy metals was mostly carried out at mercury-film electrodes (MFE). However, because of the toxicity of mercury, future regulations and occupational health consideration may severely restrict the use of mercury. In search for alternative electrode materials, just above mentioned BDD electrodes have been shown to offer more preferable performance to MFE for anodic stripping voltammetric measurements of trace metals (Langeloth *et al.*, 2010; McGaw, Swain, 2006). Mainly the electrochemical behaviors of diamond electrodes in aqueous electrolytes have been investigated (Pecková *et al.*, 2011). The most important properties of this electrode are a large potential window, lower adsorption, corrosion stability in very aggressive media, high efficiency in oxidation processes, very low double-layer capacitance and background current (Pecková *et al.*, 2009). Also, thanks to these properties, conducting diamond seems to be a promising electrode material and so, in the last decades, it has been studied with the goal of developing applications in three broad areas: electro-synthesis, electro-analysis and sensor technology; and water treatment (Fardel *et al.*, 2006; Griesbach *et al.*, 2005). The experimental results indicated that BDD electrode exhibited more attractive voltammetric response to Zn(II) than the bismuth film electrode. The present work suggests a new speedy, precise and accurate analytical procedure for the determination Zn(II) by anodic stripping voltammetry at BDD electrode surface.

## Materials and Methods

The voltammetric measurements were carried out using Autolab PGSTAT-302N (Metrohm Autolab B.V., The Netherlands) potentiostat/galvanostat controlled with the NOVA 1.6 software. All the electrochemical experiments were conducted in a three electrode single

compartment glass cell. An Ag/AgCl (3.0 mol L<sup>-1</sup> KCl) electrode was used as reference and the counter electrode was a Pt wire. The working electrode was BDD (Windsor Scientific Ltd., United Kingdom) with inner diameter of disc of 3 mm. As a supporting electrolyte 0.1 mol L<sup>-1</sup> KCl was used.

The voltammetric cell was kept at 20.0±0.5 °C. Oxygen was removed by bubbling pure nitrogen through the solution for 10 min. All reagents were used as received without any further treatment. Standard stock solution of Zn(II) was prepared by dissolution of high purity (99.5 %) ZnSO<sub>4</sub>·7H<sub>2</sub>O (Lachema, Brno) in deionized water. In All subsequent solutions were made using deionized water of with resistivity no lower than 18 μΩ cm<sup>-1</sup> (Eurowater, Bratislava). The working calibration solutions of lower concentrations were freshly prepared by using dilution method.



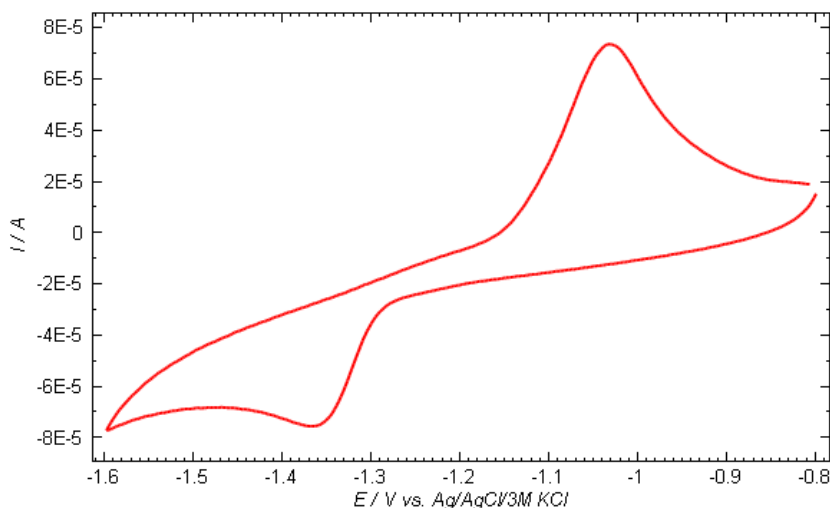
**Fig. 1.** Construction of BDD electrode, 1: electric contact, 2: body of electrode, 3: silicon plate with diamond film, 4: active surface of electrode.

The calibration curve was measured at least five times and the dates were evaluated by linear regression. The limit of detection (quantification) was calculated as three (ten) times the standard deviation of intercept divided by the slope of the linear regression.

## Results and Discussion

In the first step it was necessary to study the electrochemical redox behavior of Zn(II)/Zn in chloride electrolyte (0.1 mol L<sup>-1</sup> KCl). As working electrode, BDD electrode has been employed. The cyclic voltammetry is most appropriate method for studying mechanism of processes occurring in the diffuse layer of the electrode and for the purposes of identification of products. It usually applies triangular (mostly symmetrical) voltage pulse. In

our case, potential was changed from  $-0.8$  V to  $-1.6$  V vs. Ag/AgCl/3M KCl. Chloride electrolyte was electrochemically inactive in this entire potential range, and at very negative potentials, reduction of proton was observed. For the purpose of cyclic voltammetry,  $1 \times 10^{-4}$  mol L<sup>-1</sup> Zn(II) was used.

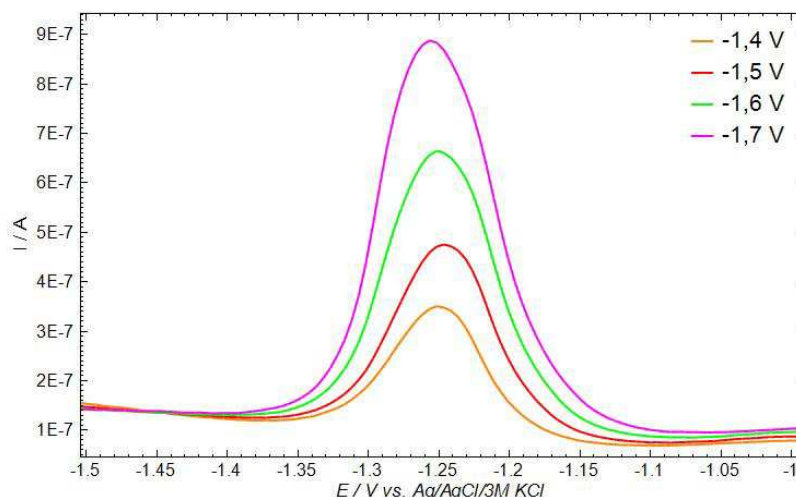


**Fig. 2.** Cyclic voltammogram  $1 \times 10^{-4}$  mol L<sup>-1</sup> Zn(II) at BDD electrode with scan rate  $100 \text{ mV s}^{-1}$ .

At the potential  $-1.36$  V vs. Ag/AgCl/3M KCl, cathodic (reduction) peak pertaining to reduction Zn(II) to Zn(0) was observed (Fig. 2). Around 200-300 mV after reduction peak, polarization was changed in the opposite direction and anodic (oxidation) peak pertaining to reoxidation the product of the cathodic electrode reaction was registered at  $-1.03$  V. We can conclude that studied redox system in chloride electrolyte on the surface of BDD electrode is irreversible as can be seen from difference (300 mV) between reduction and oxidation peak potential. To assess the reversibility of electrode reactions it could be used also the ratio of peak of anodic and cathodic current.

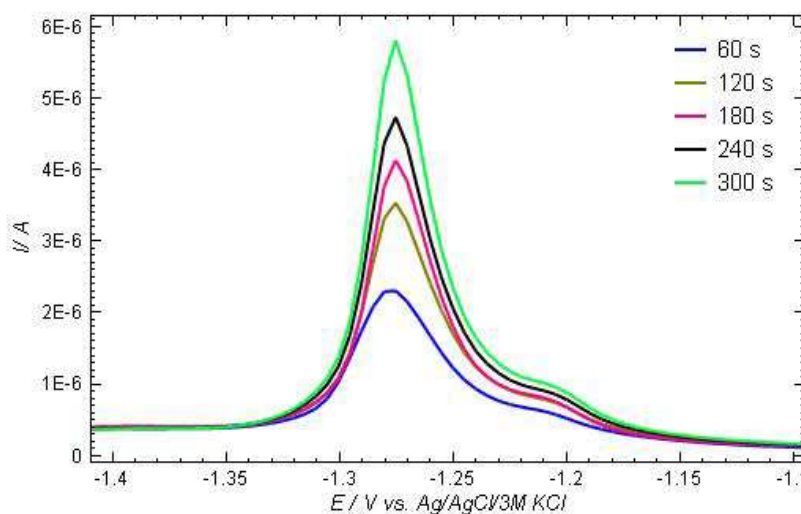
Differential pulse anodic stripping voltammetry (DPASV) is suitable electrochemical method for the determination of Zn(II). The peak current obtained in differential pulse voltammetry is dependent on various instrumental parameters such as modulation amplitude, modulation frequency and step potential. These parameters are interrelated and affect the response, but here only the general trends were examined. It was found that these parameters had little effect on the peak potential. The results of this optimization study show that the set of modulation amplitude of 25 mV, modulation time of 50 ms and step potential of 5 mV are best suited for the determination of Zn at BDD electrode. The influence of deposition

potential and time on the peak current has been examined and the optimal conditions have been set up for the detection of Zn. The solution of  $1 \times 10^{-7}$  mol L<sup>-1</sup> Zn(II) was exposed to four different deposition potentials (-1.4, -1.5, -1.6 and -1.7 V) for 120 s. The stripping peak changed significantly from each potential and the maximal height was observed at potential -1.7 V (Fig. 3).



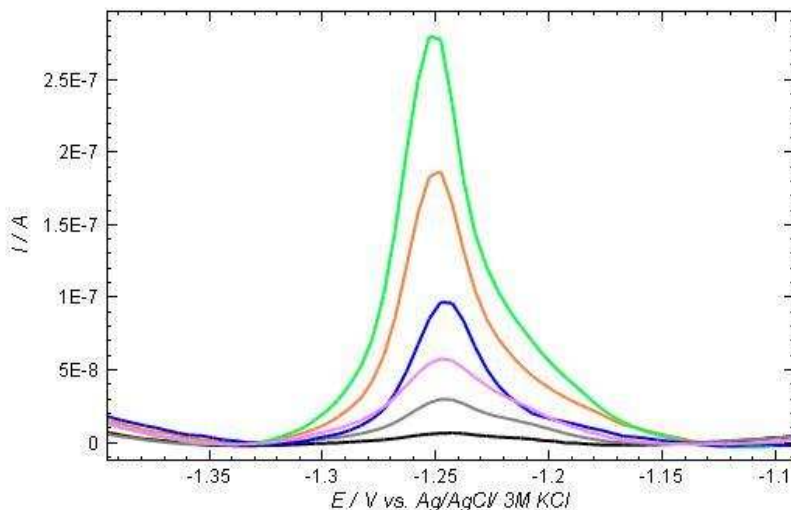
**Fig. 3.** DPASV voltammograms of  $1 \times 10^{-7}$  mol L<sup>-1</sup> Zn(II) at different deposition potentials.

It is obvious that longer deposition times increased the peak current because more Zn could be deposited during longer deposition steps. The deposition time was investigated only within a range of 60-300 s (Fig. 4) at potential -1,7 V. According to the trend, the time of 300 s might result in the highest peak current. However, we did not conduct the experiment with a deposition time longer than 300 s in order to keep the time for one measurement short.



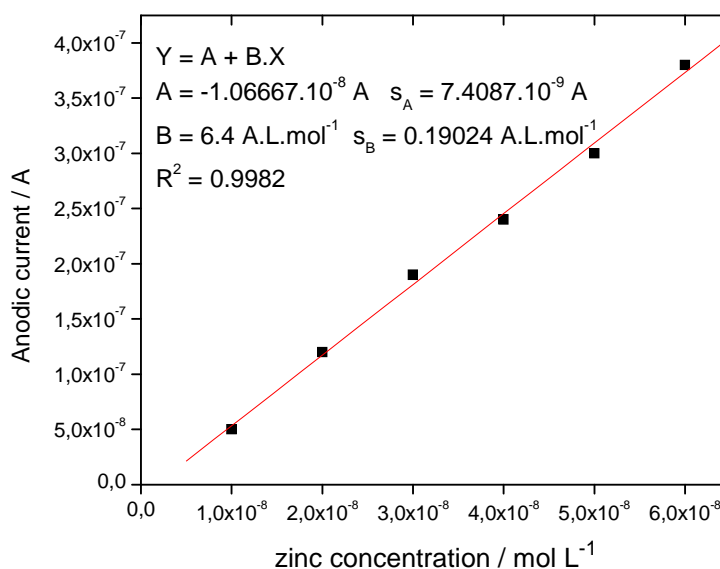
**Fig. 4.** DPASV voltammograms of  $1 \times 10^{-7}$  mol L<sup>-1</sup> Zn(II) at different deposition times.

After optimization, the experiments were carried out with deposition potential of  $-1.7$  V, deposition time was 300 s (with stirring). The deposited zinc was then stripped off at a scan rate of  $100 \text{ mV s}^{-1}$  up to the potential of  $-1.1$  V.



**Fig. 5.** DPASV voltammograms of the anodic stripping response to series of calibration solutions ( $1, 2, 3, 4, 5$  and  $6 \times 10^{-8} \text{ mol L}^{-1}$  with increasing current peak in this order) of Zn(II).

The next experiment was carried out with all the optimized conditions and settings. The series of calibration solutions of  $1, 2, 3, 4, 5$  and  $6 \times 10^{-8} \text{ mol L}^{-1}$  Zn(II) have been prepared. Well-defined stripping peaks are seen for all the concentration levels (Fig. 5). From the parameters of linear regression (Fig. 6), limit of detection and limit of quantification were estimated ( $3 \times 10^{-9}$  and  $1 \times 10^{-8} \text{ mol L}^{-1}$ , respectively).



**Fig. 6.** Calibration curve with parameters of linear regression.

## Conclusion

The measurement described in this paper offers a simple and inexpensive way to detect zinc. The detection limit of zinc reported in this paper shows that BDD can be used for a broad variety of applications and can displace old toxic Hg-electrodes or expensive and complex spectrographic methods. For a higher sensitivity, the extension of deposition time still offers further possibilities to decrease the detection limit. However, further mechanistic studies are recommended in order to understand the processes on the BDD surface and to confirm the assumption.

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## References

- Broadley MR, White PJ, Hammond JP, Zelko I, Lux A (2007) *New Phytol.* 173: 677-702.
- Fardel R, Griesbach U, Pütter H, Comninellis C. (2006) *J. Appl. Electrochem.* 36: 249-253.
- Galgano F, Favati F, Caruso M, Scarpa T, Palma A (2008) *Food Sci. Technol.* 41: 1808-1815.
- Griesbach U, Zollinger D, Pütter H, Comninellis C. (2005) *J. Appl. Electrochem.* 35: 1265-1270.
- Halicz L, Becker JS, Pickhardt C, Gavrieli I, Burg A, Nishri A, Platzner IT (2006) *Int. J. Mass Spectrom.* 249-250: 296-302.
- Jones SEW, Chevallier FG, Paddon CA, Compton RG (2007) *Anal. Chem.* 79: 4110-4119.
- Langeloth M, Chiku M, Einaga Y (2010) *Electrochim. Acta* 55: 2824-2828.
- Madejczyk M, Baralkiewicz D (2008) *Anal. Chim. Acta* 617: 11-17.
- McGaw EA, Swain GM (2006) *Anal. Chim. Acta* 575: 180-189.
- Pecková K, Barek J (2011) *Curr. Org. Chem.* 15: 3014-3028.
- Pecková K, Musilová J, Barek J (2009) *Crit. Rev. Anal. Chem.* 39: 148-172.