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Original Research

Boron-Doped Diamond Electrode as Sensitive and Selective Green Electroanalytical Tool for Heavy Metals Environmental Monitoring: Zinc Detection in Rubber Industry Waste

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Abstract

A simple and sensitive electroanalytical technique for the detection and quantification of zinc has been developed that demonstrates beneficial analytical features of boron-doped diamond electrode. The influence of deposition potential on the stripping peak current of zinc was studied, and optimum value of -1.7 V vs. Ag/AgCl electrode was chosen. Optical and atomic force microscopic studies showed that the mechanism of deposition process is governed by nucleation by which first nanoparticles and then grains of zinc are formed. The detection limit of 4.7×10^{-10} mol·l^{-1}, good repeatability (relative standard deviation of 3.2%) as well as wide linear dynamic range from 5×10^{-10} to 5×10^{-6} mol·l^{-1} were obtained in 0.1 mol·l^{-1} KCl for deposition time of 120 s. Interference from other heavy metals such as Hg^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} do not significantly influence anodic stripping peak of zinc even in a 100-fold excess. The method was applied in analysis of zinc in environmental rubber industry samples with results in good agreement with those obtained by atomic absorption spectrometry, confirming that the boron-doped diamond electrode is an excellent sensing tool for heavy metals environmental monitoring.

Keywords: zinc, boron-doped diamond electrode, stripping voltammetry, rubber waste

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Introduction

Zinc is an important heavy metal in nature, especially from biological and ecotoxicological points of view. It plays an important role in the synthesis of nucleic acids and proteins and biomembrane stabilization, as well as in the metabolism of sacharides. Its deficiency may result in severe illnesses like diabetes or risk enhancement of heart attack [1]. A high amount of zinc has been found in human tissues infected by cancer, Parkinson's, or Alzheimer's diseases. A significant intake of zinc may arise from the food chain, because zinc waste has the ability to be accumulated in various ecosystems, therefore its monitoring in the environment is useful and needed. Circulation and zinc bioaccumulation into water organisms has been rigorously tracked with isotopically enriched tracers [2].

Various analytical techniques for the determination of zinc in biological and environmental matrices have been developed in the last decade. The fluorimetric method [3] for the detection of trace amount of zinc based on the reaction with 3-hydroxyflavone as fluorophore agent with a detection limit (LOD) of 1.5 ppb (2.3×10^{-8} mol·l^{-1}) has recently been reported. Spectrophotometric determination is based on zinc reaction with a chelate-producing colored extractable complex of which absorbance is measured [4]. This technique is highly selective, and the detection limit is 1-2 orders lower than in the case of fluorimetric techniques. The extraction step may be time-consuming unless the ultrasound is introduced to the system [5].

However, the most popular techniques of determination of zinc are atomic absorption spectrometry (AAS) [6] with a detection limit of 6×10^{-8} mol·l^{-1}, with flame atomization [7] (LOD = 1×10^{-7} mol·l^{-1}) and ICP-AES or ICP-MS [8] (LOD = 5×10^{-9} mol·l^{-1}) which are fast, selective, and well automated. When samples like marine sediments contain high amount of salts, they usually may remain in spectrometer jets and obstruct the vaporization process. Beneficial features for solving this problem lie in an online connection of atomic spectrometry with electrochemistry in a flow system bringing the synergetic effect of metal preconcentration on the electrode surface together with matrix washing by changing the supporting electrolyte with acceptable properties for AAS [9].

The fundamentals of electrochemical methods for zinc detection reside in the fact that zinc ions can be cathodically reduced to metal, thus allowing accumulation on the electrode surface. In this point of view mercury-based electrodes are very sensitive due to amalgam formation and usually are used for zinc detection by anodic stripping voltammetry [10]. A detection limit of 10^{-11} mol·l^{-1} can be achieved for long deposition times. In recent times a pressure for total prohibition of mercury [11] due to its toxicity has appeared to be stimulating, thus scientific attention is paid to solid stationary electrodes. Except platinum [12], gold [13], bismuth [14], and antimony [15], various types of solid electrodes based on carbon have been utilized for zinc determination. Screen-printed carbon electrodes [16] and carbon nanotubes [17], as well as glassy carbon [18] or carbon paste [19] electrodes are less sensitive in comparison with mercury electrodes, and the voltammetric signal is affected by hydrogen evolution due to the rather negative potential of cathodic reduction of zinc. Bubbles of generated hydrogen during zinc accumulation may be effectively removed by cavitational streaming from an ultrasound probe placed in a close vicinity to a glassy carbon electrode surface [18].

In this study we present a novel differential pulse anodic stripping voltammetric (DPASV) technique for the determination of zinc in waste from the rubber industry based on use of boron-doped diamond (BDD) electrode as a green electroanalytical tool, which has an extended potential window and very low background current as well as high stability in aggressive media [20].

Experimental Procedures

Morphological Characterization of Stripping Process on BDD Surface

The topological optical images of BDD electrode surface with and without deposited zinc film were characterized with an optical guidance microscope in an atomic force microscopy (AFM) Veeco CPII probe at the recognition of 400×300 μm. AFM measurements were performed with the same instrument in contact and noncontact mode. A standard silicon nitride tip with radius of 10 nm (Contact mode: force 100 nN, force constant k<1 N·m^{-1}; Noncontact mode: vibration frequency 285 kHz, set point of 45 nm, force constant k = 20-80 N·m^{-1}) was used. Scans were recorded at a frequency of 1 Hz.

Electrochemical Measurement Procedures

All electrochemical experiments were conducted in a three-electrode single-compartment glass cell kept at 20.0±0.5ºC. A classic commercially-available boron-doped diamond electrode (Windsor Scientific Ltd., United Kingdom) with an inner diameter disc of 3 mm served as the working electrode. An Ag/AgCl (3 mol·l^{-1} KCl) electrode was used as reference and Pt wire as a counter electrode. Voltammetric measurements were carried out with an Autolab PGSTAT-302N (Metrohm Autolab B.V., The Netherlands) potentiostat/galvanostat controlled with NOVA 1.8 software. Oxygen was removed by bubbling pure nitrogen through the solution for 10 min. All reagents were used as received without any further treatment.

Chemicals and Real Samples

As a supporting electrolyte 0.1 mol·l^{-1} KCl (Lachema, Brno) was employed. All solutions were made using deionized water with resistivity above 18 μΩcm (Eurowater, Bratislava). Standard stock solution of Zn^{2+} was prepared from high pure (99.5%, w/w) $ZnSO_4\cdot7H_2O$ (Lachema, Brno) in deionized water. The working calibration solutions of lower concentrations were freshly prepared by further dilution with the supporting electrolyte.

The rubber waste pieces from tire production, waste water, and river water served as real samples. 1 g of rubber waste was weighed, cut on smaller parts, and ashed in the furnace at 550ºC for two hours. Inorganic residua were then dissolved in a platinum crucible with warm concentrated hydrochloric acid (20 ml). After cooling and transfer to the 250 ml volumetric flask, the solution was filled at the mark with 0.6 mol·l^{-1} K_2CO_3 to neutralize the sample and to form KCl as the supporting electrolyte. From this solution 1 ml was pipetted to an electrochemical cell containing 19 ml of 0.1 mol·l^{-1} KCl. Waste and river water samples were analyzed directly: 1 ml of water sample was pipetted into an electrochemical cell containing 19 ml 0.1 mol·l^{-1} KCl.

Results and Discussion

Morphological Characterization and Mechanism of Zn Deposition on BDD Surface

As a first step, the morphology characterization of Zn deposition onto BDD surface placed on a flat teflon pad with optical microscopy was performed. It can be seen in Fig. 1 that the deposition process is based on progressive nucleation, because several tens of thousands of nuclei per cm^2 were found for 1×10^{-7} mol·l^{-1} of Zn^{2+} solution deposited at -1.7 V vs. Ag/AgCl electrode for 120 s. The deposition is inhibited in the presence of surfactants due to the occupation of nucleation centers with hydrophobic parts of their molecules. This fact is consistent with previous results [21] for deposition of Cd^{2+} ions in acetate buffer at -1.8 V vs. Ag/AgCl electrode.

Mechanism of the Zn deposition was investigated also by *ex-situ* AFM microscopy. As confirmed by Fig. 2, at higher concentrations of Zn^{2+} ions the Zn film has "islands of grain" morphology. This morphology is typical for various heavy metals deposited on the BDD electrode [21]. The islands of zinc film are thicker with lower relative height in comparison with zinc deposition at lower concentration. Very thin islands with substantially higher relative height were obtained in *ex-situ* AFM experiment for 1×10^{-9} mol·l^{-1} solution of Zn^{2+}. This is attributed to Zn nanoparticles formation as a first step of the nucleation process. During the next phase of the deposition process its diameter is growing and they are merging with each other to format the grain structure of zinc film (Fig. 3A and 3B). To avoid possible

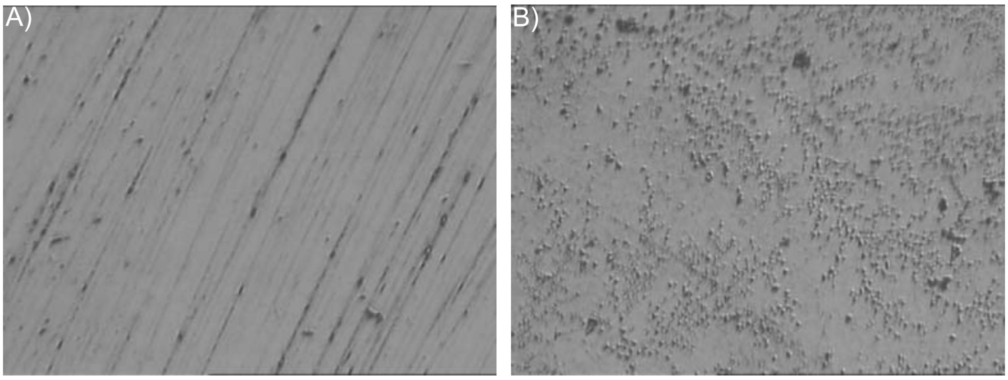

Fig. 1. (A) Optical image for a bare BDD electrode, (B) optical image for deposited zinc on BDD electrode. Images were recorded at 1×10^{-7} mol·l^{-1} solution of Zn^{2+} ions in 0.1 mol·l^{-1} KCl as supporting electrolyte after deposition time of 120 s at deposition potential of -1.7 V vs. Ag/AgCl electrode. Both images are 400×300 μm.

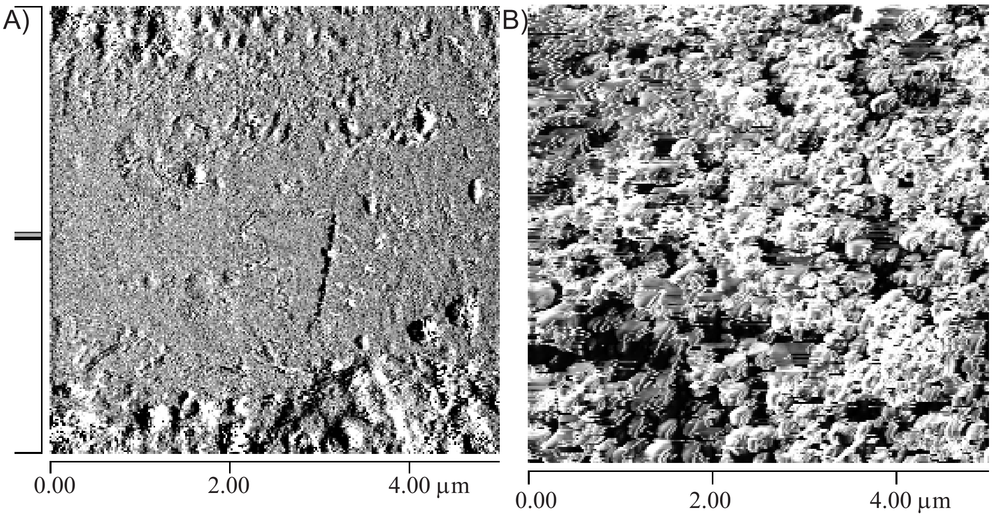

Fig. 2. (A) AFM image of bare BDD electrode, (B) Typical *ex-situ* AFM image of BDD electrode with deposited zinc film. Image recorded from 1×10^{-7} mol·l^{-1} of Zn^{2+} ions in 0.1 mol·l^{-1} KCl as supporting electrolyte after deposition time of 120 s at deposition potential of -1.7 V vs. Ag/AgCl electrode.

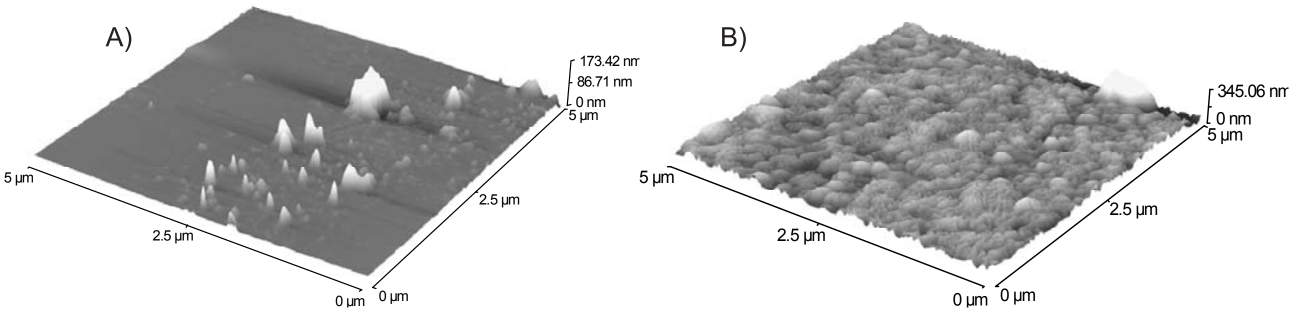

Fig. 3. (A) *Ex-situ* AFM 3D image of zinc nanoparticles formatted from 1×10^{-9} mol·l^{-1} Zn^{2+} solution, (B) *ex-situ* AFM 3D image of grain morphology for zinc deposition from 1×10^{-7} mol·l^{-1} Zn^{2+} solution. Conditions: 0.1 mol·l^{-1} KCl as supporting electrolyte, deposition time of 120 s, deposition potential of -1.7 V vs. Ag/AgCl electrode.

incomplete removal [21] of zinc during the stripping step it is recommended to clean and activate the BDD electrode with highly positive potential more than 2.5 V vs. Ag/AgCl electrode for at least 30 s.

Electrochemical Behavior of Zinc on BDD Electrode Surface

In the next step we investigated electrochemical behavior of Zn^{2+} ions on BDD electrode by cyclic voltammetry at a scan rate of 100 mV·s^{-1}. Potassium chloride (KCl) was chosen as the supporting electrolyte, because it is well known that zinc ion are easy to reduce to metallic zinc in this media on various electrode materials, including mercury or carbon. As can be seen from Fig. 4 (dashed line) 0.1 mol·l^{-1} KCl without Zn^{2+} has a very low (a few nA) signal on BDD electrode in the potential range from -0.7 to -1.6 V vs. Ag/AgCl electrode. We also observed high hydrogen overpotential, because bubbles of electrogenerated hydrogen did not occur even at highly negative potentials of more than -2 V vs. Ag/AgCl electrode. This value is significantly higher than in the case of glassy carbon electrode, where bubbles of hydrogen occur nearly behind Zn^{2+} ion reduction, thus complicating its deposition onto the electrode surface. However, a cyclic voltammogram of 1×10^{-5} mol·l^{-1} Zn^{2+} solution in 0.1 mol·l^{-1} KCl shows a well-developed reduction peak at -1.37 V vs. the Ag/AgCl electrode, indicating that zinc film is formed without the influence of hydrogen bubbles and at -1.07 V vs. the Ag/AgCl electrode an anodic stripping peak of deposited zinc film was found. This peak is very sensitive to time, at which potential is kept on value corresponding to zinc film deposition, and is very repeatable because from 10 consecutive runs the relative standard deviation of 3% was calculated for peak current magnitude. Furthermore, a detection limit of 1×10^{-6} mol·l^{-1} was obtained in these conditions without the accumulation step. Concluding these facts, it may be said that BDD electrode might be very advantageous for zinc detection from the sensitivity and repeatability point of view.

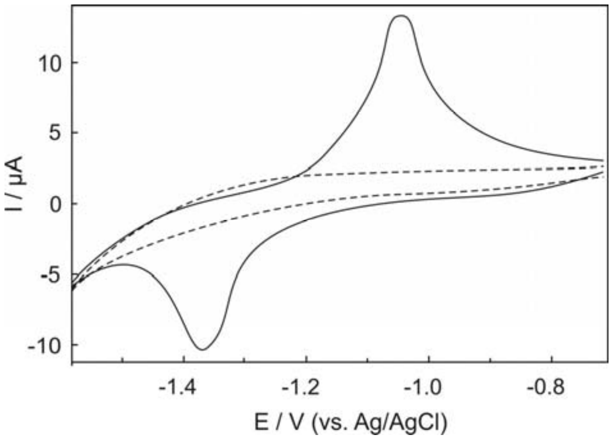

Fig. 4. Cyclic voltammograms of (---) 0 mol·l^{-1} and (—) 1×10^{-5} mol·l^{-1} Zn^{2+} in 0.1 mol·l^{-1} KCl on BDD electrode with starting potential of -0.7 V vs. Ag/AgCl electrode and scan rate of 100 mV·s^{-1}.

Optimization of Deposition Potential

Deposition potential is an important parameter for stripping techniques that influences the sensitivity of the determination. Because cyclic voltammetry belongs to less sensitive voltammetric techniques, we switched our investigations to differential pulse anodic stripping voltammetry (DPASV) experiments. The influence of deposition potential on the stripping peak current magnitude of zinc was examined in the range from -1.4 to -1.8 V vs. Ag/AgCl electrode and the optimum value has been set up for the quantification of zinc. DPAS voltammograms were recorded from the particular deposition potential to -0.8 V vs. Ag/AgCl electrode after deposition time of 120 s with stirring, and used by optimized DPASV instrumental parameters (pulse amplitude of 100 mV, pulse width of 50 ms and scan rate of 25 mV·s^{-1}). As can be seen from Fig. 5, a peak current magnitude increased when deposition potential was higher than -1.4 V to -1.7 V vs. Ag/AgCl, at which it reaches maximum value. At more negative values of the deposition potential the voltammetric signal is decreased, probably due to slight hydrogen bubble generation. Therefore, deposition potential of -1.7 V vs. Ag/AgCl electrode was chosen as optimum value in further voltammetric experiments. We determined that the deposition time of 120 s is satisfactory in order to keep the time of one voltammetric measurement short and effective.

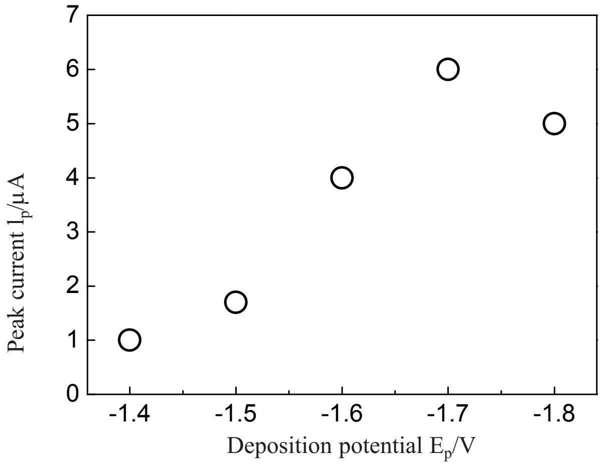

Fig. 5. Dependence of peak current magnitude on deposition potential at 1×10^{-7} mol·l^{-1} Zn^{2+} in 0.1 mol·l^{-1} KCl. DPASV conditions: pulse amplitude of 100 mV, pulse width of 50 ms, scan rate of 25 mV·s^{-1} and deposition time of 120 s.

Analytical Characteristics

Next, the sensitivity of DPASV response to additions of Zn^{2+} was investigated. Each DPAS voltammogram (Fig. 6A) was measured six times with good repeatability. Relative standard deviation of the above-mentioned consecutive runs did not exceed 3.2%. It was observed that peak (Fig. 6B) current magnitude linearly (R^2= 0.992) depends on Zn^{2+} concentration in the concentration range from 5×10^{-10} to 1×10^{-8} mol·l^{-1}. The dependence fits the equation, $I = a + b\times c$, with the intercept $a = 6\times10^{-8}$ A (s_a= 9×10^{-9} A) and the slope b = 60 A l·mol^{-1} (s_b = 2 A l·mol^{-1}). Based on these analytical performance characteristics a detection limit of 4.7×10^{-10} mol·l^{-1} was estimated using $3s_a/b$ criterion. This value is lower than for other electrode materials. For further optimation of measurement conditions especially for very long deposition times, a detection limit of a few picomoles per liter might be expected. In the next experiment linearity of signal was observed over concentration range from 5×10^{-10} to 5×10^{-6} mol·l^{-1}, representing dynamic linear concentration range of the technique.

Interference Study

BDD electrode is also very sensitive for other heavy metal cations that electrochemically accumulate on the electrode surface as metals and then strip down back to the solution. Especially Hg^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} may be present in environmental samples and may affect detection of zinc; therefore, we performed an interference study. As can be seen from Fig. 7 DPASV signals of possible interfering metal cations are well separated over the wide potential range and do not affect the signal of zinc even at 100-fold excess. No possible interfering intermetalic compounds and microdrops of Hg film were also observed during these experiments.

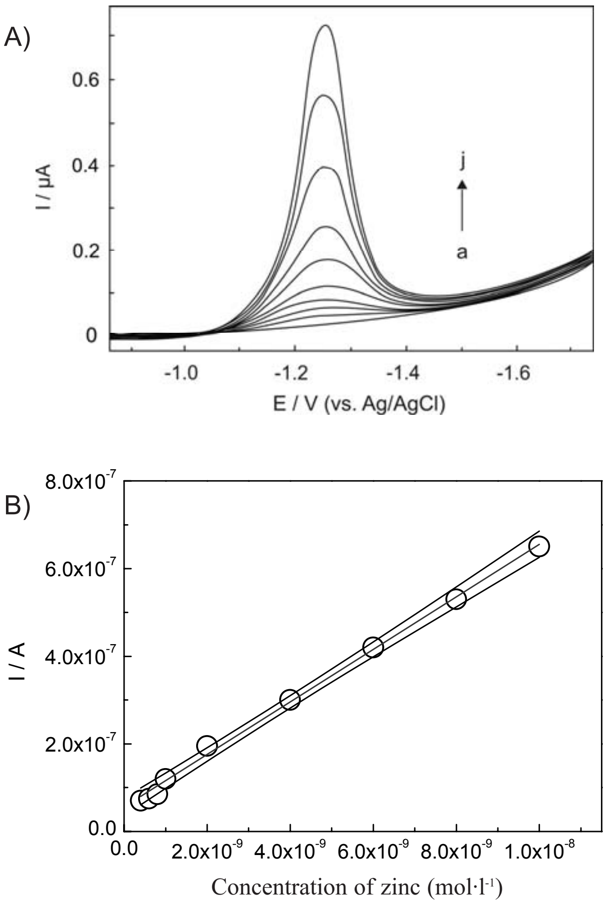

Fig. 6. (A) DPAS voltammograms of blank (curve a) and 9 standard additions (curves b to j); each addition was 2 μl (1×10^{-5} mol·l^{-1}) Zn^{2+} on BDD electrode. DPASV conditions: deposition potential of -1.7 V vs. Ag/AgCl electrode, deposition time of 120 s, pulse amplitude of 100 mV, pulse width of 50 ms, and scan rate of 25 mV·s^{-1}. (B) Dependence of peak height vs. concentration of zinc (taken from (A)) with regression line and confidence interval for 95% probability.

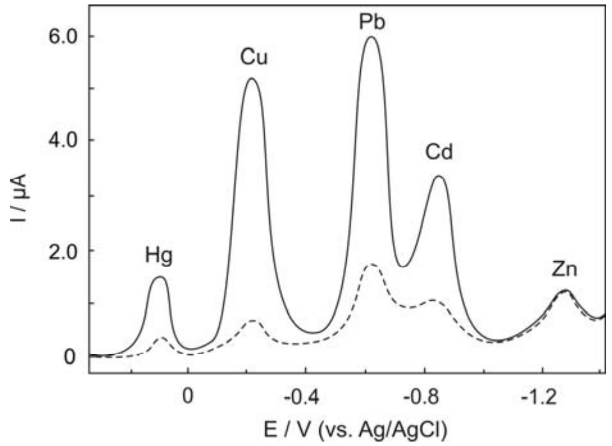

Fig. 7. DPAS voltammograms representing signal of 1×10^{-8} mol·l^{-1} Zn^{2+} solution in 0.1 mol·l^{-1} KCl on BDD electrode in the presence of other heavy metals as possible interfering agents. Dashed line: Hg^{2+} (1×10^{-7} mol·l^{-1}) and Cu^{2+}, Pb^{2+}, and Cd^{2+} (1×10^{-8} mol·l^{-1}); Full line: Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+} in 100-fold excess (all 1×10^{-6} mol·l^{-1}). DPV conditions: deposition potential of -1.7 V vs. Ag/AgCl electrode, deposition time of 120 s, pulse amplitude of 100 mV, pulse width of 50 ms, and scan rate of 25 mV·s^{-1}.

Table 1. Model samples analysis of zinc (number of analysis was n=6).

Taken	Found	SD	Confidence interval for 95% probability*	
ng	ng	ng	ng	%
13.0	15.0	1.8	1.9	12.7
25.0	22.0	2.6	2.7	12.3
40.0	36.0	4.0	4.2	11.7
53.0	56.0	6.1	6.4	11.4

*Calculated according to the formula $t_{n-1,\ \alpha}$ SD/sqrt(n); $t_{5;0.05}$=2.5706

Table 2. Real samples analysis of zinc (n=4 for both methods).

Sample	Zn content* mg·kg^{-1}	SD mg·kg^{-1}	Zn content** mg·kg^{-1}	SD mg·kg^{-1}
A	1.5×10^{6}	1.8×10^{5}	1.8×10^{6}	1.9×10^{5}
B	8	1	10	1
C	45	5	42	4

A – Rubber waste pieces from Continental Matador Rubber Company, Púchov, Slovakia, B – River water (sample taken from Váh river near city Púchov), C – Waste water
*determined by proposed method
**determined by AAS as reference independent technique

Model and Real Samples Analysis

To complete validation of the proposed method, a model samples analysis was performed. The results are summarized in Table 1. Four samples of 20 ml solutions with an absolute Zn^{2+} content of 13, 25, 40, and 53 ng with 100-fold excess of Hg^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} were analyzed. Multiple standard addition method was used in all analyses. The mean of six parallel determinations does not statistically differ from taken values and relative halfwidth of 95% confidence interval also is acceptable (taking into account the very low content of the target analyte).

To demonstrate practical applicability of the proposed technique, real samples analysis was performed. Pieces of rubber waste from tire production containing zinc oxide as an accelerator of an vulcanization process, river water containing natural zinc and waste water contaminated with zinc from old tire stock ground were chosen as real samples. The results of real sample analysis are given in Table 2 and were compared with AAS results chosen as reference independent analytical technique due to its reliability for this kind of analysis. A statistical results agreement between proposed and reference independent technique was reached, as well as acceptable precision represented by low standard deviation (SD) values. The results introduced in this paper offer a simple and inexpensive way to detect and quantify zinc content.

Conclusions

A boron-doped diamond (BDD) electrode was used in the development of sensitive and selective analytical technique for zinc detection. Deposition of zinc onto BDD electrode surface was studied with optical and AFM microscopy showing the nucleation mechanism, and from nanoparticles to grain zinc film growth. At optimized experimental conditions a detection limit of 4.7×10^{-10} mol·l^{-1} was estimated by using $3s_A/B$ criterion for the relatively short time of zinc deposition as well as linear dynamic concentration range from 5×10^{-10} to 5×10^{-6} mol·l^{-1}. The proposed method is selective because other heavy metals like Hg^{2+}, Cu^{2+}, Pb^{2+}, and Cd^{2+} as possible interferents do not influence stripping peak of zinc even at 100-fold excess. The method was applied for analysis of environmental samples from the rubber industry. By this study we would like to demonstrate that BDD can be used as green and sensitive electrode material for heavy metals environmental monitoring and can replace toxic mercury electrodes or complex and expensive spectral methods.

Acknowledgements

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