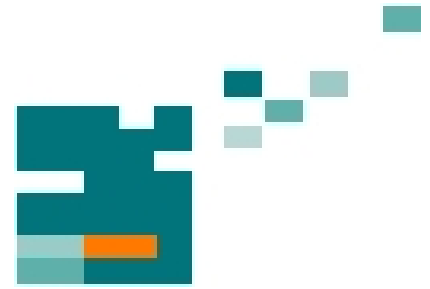**54. IWK**

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TECHNISCHE UNIVERSITÄT ILMENAU

AN EFFECT OF BISMUTH FILM ELECTROPLATING VARIABLES ON ELECTRODE PERFORMANCE IN ELECTROANALYSIS

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ABSTRACT

Bismuth film electrodes (BiFEs) have a potential to replace toxic mercury used most frequently for determination of heavy metals (Cd, Pb, Zn) by anodic stripping voltammetry. We prepared a graphite disc electrode (0.5 mm in diameter) from a pencil-lead rod and developed a nitrogen doped diamond-like carbon (NDLC) electrode on a highly conductive silicon substrate as a support for BiFEs. The disc graphite BiFE was used for simultaneous determination of Pb(II), Cd(II) and Zn(II) by square wave voltammetry (SWV) in an aqueous solution. We found the optimum bismuth-to-metal concentration ratio in the solution to be 20. The dependence of the stripping responses on the concentration of target metals was linear in the range from 1×10^{-8} to 1.2×10^{-7} mol/L. A bismuth-plated NDLC electrode was used for Pb(II), Cd(II) and Zn(II) determination by SWV in an aqueous solution. We found that the stripping current for bismuth-plated NDLC electrode was linear in the concentration range of target metals in solution from 2×10^{-8} to 6×10^{-8} mol/L only. At a higher concentration has been observed saturation of signal.

Index Terms - Anodic stripping voltammetry, Diamond-like carbon, Bismuth film electrode

1. INTRODUCTION

General trends for environmentally friendly analytical methods and alternative materials have continuously been sought. From this point of view bismuth film electrodes are very promising in the field of electrochemical analysis. Bismuth has a potential to replace toxic mercury used most frequently for determination of heavy metals (such as Cu, Cd, Pb, Zn) by anodic stripping voltammetry (ASV) [1, 2]. The attractive properties of bismuth films include simple preparation, high sensitivity, excellent peak resolution, insensitivity to dissolved oxygen in aqueous solutions, negligible toxicity and ability to operate in highly alkaline media [3-5].

Anodic stripping voltammetry is a very attractive electroanalytical technique for determination of trace heavy metals. The method is characterized by remarkable sensitivity and extremely low detection limits (< ppb). Other advantages such as the ability to determine simultaneously several metals with high selectivity, rapidity, simplicity and low cost of the analyses are important. The high sensitivity and low detection limits are mainly given by the first step involving preconcentration of the analyte species in accumulating metal (bismuth or mercury), which is carried out under a fixed reduction potential for a predetermined time. In the second, stripping step, the accumulated species are stripped from bismuth or mercury into the solution by reoxidation. The stripping current peaks are proportional to the concentration of the species accumulated in bismuth or mercury and, hence, to the concentration in the analyte.

Toxic metals can simultaneously be determined for concentration levels down to sub-ppb. The stripping step can involve a variety of potential waveforms. Pulse techniques such as differential pulse voltammetry (DPV) and mainly square wave voltammetry (SWV) are preferred rather than linear-potential scan techniques. In addition, the stripping analysis by SWV eliminates the time-consuming deaeration step because the stripping step is less sensitive to irreversible processes at high square wave frequency, such as the reduction of oxygen which is dissolved in aqueous solutions [6, 7]. Thanks to this technique, the oxygen interference with analytical signal is strongly reduced.

There are two methods which are the most frequently used. The first method, *ex-situ* plating, involves electroplating the accumulating metal before transffering the electrode into the analyzed solution [3, 5]. In the second method, *in-situ* plating, bismuth or mercury ions are added into the analyzed solution and target metals are co-deposited with bismuth or mercury on the electrode. The latter procedure is usually recommended because it gives better ASV performance in terms of sensitivity, selectivity and reproducibility. Another advantage of *in-situ* technique is the new surface generated at each analysis [8]. On the other hand, *in-situ* procedure cannot be employed when additions of accumulating metal into the analyte cause contamination, precipitation or changes in the speciation of the

sample [9]. In the case of *ex-situ* procedure with mercury the stability of preplated mercury can be, in comparison with bismuth, strongly influenced by experimental and storing conditions or during the transfer. Mercury microelectrodes have to be stored in a deoxygenated solution at a negative potential to prevent oxidation of mercury which causes a decrease of their performance in time [9, 10].

In general, the performance of anodic stripping voltammetry with accumulating metal film is strongly affected by the supporting electrode material. An ideal electrode should possess low ohmic resistance, chemical and electrochemical inertness, good mechanical properties, high hydrogen and oxygen overvoltage (wide potential window), low background current, ease of reproduction of the electrode surface. The choice of the electrode support that bismuth or mercury is deposited onto is crucial. Bismuth can be plated on the same substrates as mercury. Glassy carbon [11-14], carbon paste [11, 15], carbon fibre [3, 16, 17], impregnated graphite [11], pencil-lead [18], gold [5, 16], platinum [5] and others [4, 5] have been reported for bismuth.

Diamond-like carbon (DLC) is a promising material for application in electroanalyses [19-22]. DLC films can be deposited at room temperature by CVD processes from the gas phase, by ion source techniques, pulse laser deposition, ion beam deposition, microwave plasma-assisted deposition, electrodeposition from organic liquids or by sputtering [23, 24]. Analytical performance of the bismuth film electrode on DLC is influenced by the properties of DLC. DLC thin films are characterized by excellent mechanical properties (high hardness, high elastic modulus), chemical inertness to any acids, alkaline solutions or organic solvents [20]. Generally, high ohmic resistivity of DLC can be decreased by using doping elements such as nitrogen during the fabrication of the DLC. When we compare doped DLC electrodes with traditionally used metal film electrodes such as Au or Pt, the DLCs are not sensitive to surface oxidation or reduction and no chemical interaction occures with metal deposits. As well, the overvoltage of DLC to hydrogen is higher than that for Au or Pt.

In this work, results of heavy metal determination by anodic stripping voltammetry with bismuth electrodes are summarized. In this field traditionaly used mercury could be replaced by attractive bismuth. A single pencil-lead graphite electrode and nitrogen-doped DLC film electrode on silicon were used as a support for BiFE formation. A survey of many parameters which influence the performance of ASV is given.

2. EXPERIMENTAL

The nitrogen-doped DLC electrodes were fabricated by vacuum pulse sputtering of graphite on highly conductive silicon substrates (0.008 - 0.024 Ωcm). The areas which act as working electrodes were defined photolithographically using a positive photoresist.

The pencil-lead graphite disc electrode was prepared from a pencil-lead rod (HB, 0.5 mm in diameter) which was inserted into a polyethylene tube and fixed by epoxy glue. The tip of this electrode (Fig. 1) was mechanically polished. Before use, the disc electrode was rinsed only with deionized water and dried. All the stock solutions were prepared from analytical grade chemicals (Bi(NO$_3$)$_3$×5 H$_2$O – 99.999 %, Pb(NO$_3$)$_2$ – 99.0 %, Cd(NO$_3$)$_2$×4 H$_2$O – 99.0 %, Zn(NO$_3$)$_2$×6 H$_2$O – 99.0 %, CH$_3$COOH – 99,8 %, CH$_3$COONa – 99.0 %,) in 18 MΩcm deionized water. A three-electrode arrangement was used in all experiments.

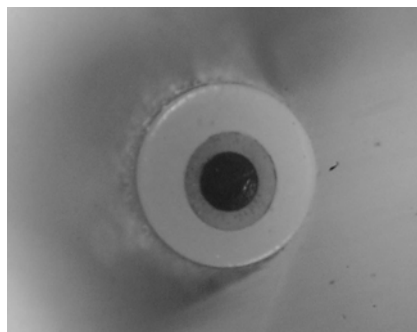*Figure 1 Single disc graphite electrode in the middle (Ø = 0.5 mm)*

As a reference, a home-made Ag/AgCl/agar Cl$^-$ (3 mol/L)/agar NO$_3^{3-}$ (1 mol/L) electrode and, as a counter electrode, a platinum wire were used. Voltammetric experiments were performed with an electrochemical sensor interface (PalmSens, Palm Instruments BV) in combination with a magnetic stirrer and personal computer. Electrochemical properties of the graphite electrodes and of the nitrogen-doped DLC electrode arrays were investigated by cyclic voltammetry (CV). SWV was used in the measurement of the stripping voltammograms. The composition of nitrogen-doped DLC films was analyzed by Raman spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Pencil-lead graphite support for bismuth film electrodes

The disc graphite BiFE was used for *in-situ* simultaneous determination of Pb(II), Cd(II) and Zn(II) by SWV in an aqueous solution.

We have found a strong effect of the SWV parameters (SW step increment, SW pulse height and SW frequency) on a response of the sensor. These parameters were investigated using a solution with Pb(II), Cd(II) and Zn(II) concentration of 1×10^{-8} mol/L of each in an 0.1 mol/L acetate buffer solution.

The effect of the step increment was investigated in the range from 2 to 30 mV (Fig. 2). The best stripping response was obtained at 12 mV step increment for Pb(II) and Cd(II), and at 25 mV for Zn(II). For all metals the peak positions as well as the peak widths were independent of the step increment.

The SW pulse height was investigated in the range from 20 to 120 mV (Fig. 3). When the pulse height increased, the stripping response gradually increased. The peak positions were shifted to the cathode direction by about 20 to 30 mV per pulse height increment (20 mV) for all metals. The peak widths were not influenced by the pulse height.

The SW frequency had a significant effect on the stripping response (Fig. 4). The peak heights for Pb(II) and Cd(II) increase up to 120 Hz. Over this frequency, the stripping responses decreased. A negligible effect of frequency on the response was found for Zn(II). The peak positions for all metals were shifted to the cathodic direction by about 10 mV per frequency increment (20 Hz). In accordance with the observed results, a step increment of 12 mV, pulse height 80 mV and frequency 120 Hz were chosen for SWV experiments with the pencil-lead graphite electrode.

The concentration of Bi(III) used for *in-situ* formation of the bismuth film on graphite electrodes is known to influence the height of the stripping peaks of the target metals [11, 14, 18]. Stripping voltammograms with the pencil-lead graphite electrode for the solution with 1×10^{-8} mol/L concentration of each of Pb(II), Cd(II) and Zn(II) in 0.1 mol/L acetate buffer are shown in Fig. 5. They were recorded at different contents of Bi(III) from 3.3×10^{-8} (bismuth-to-metals ratio of 3.3:1) to 1×10^{-6} mol/L (bismuth-to-metals ratio of 100:1). In Fig. 6 there are shown the dependences of the stripping current on the concentration ratio of Bi(III) to metals in the solution. As the Bi(III) concentration increased, all the peaks increased in height up to a ratio of 20:1. After a slight decrease for Cd(II) and Zn(II) peaks, the current responses of all metals became independent of additional increasing of Bi(III).Hz
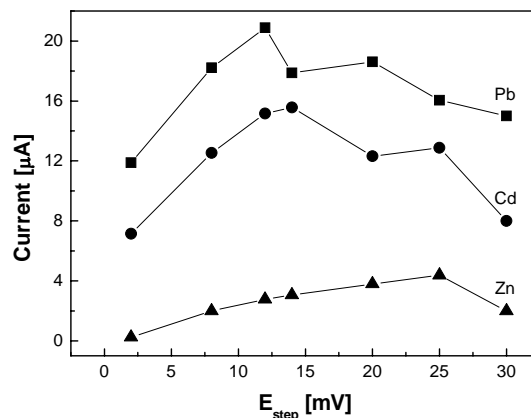
were chosen for SWV experiments with the pencil-lead graphite electrode.

Figure 2 Dependence of current response on step increment of SWV in 0.1 mol/L acetate buffer; concentration of each of metals: 3×10^{-7} mol/L, Bi(III): 1×10^{-6} mol/L, preconcentration time: 60 s
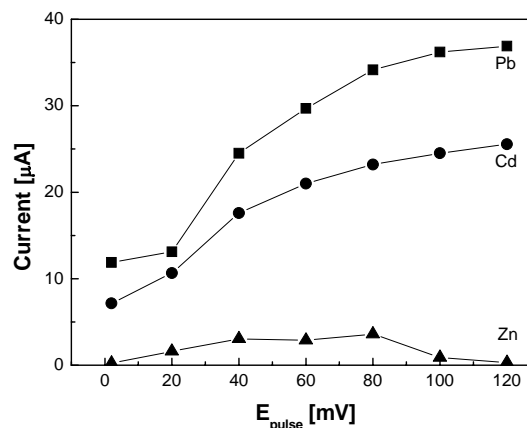

Figure 3 Dependence of current response on pulse height of SWV in 0.1 mol/L acetate buffer; concentration of each of metals: 3×10^{-7} mol/L, Bi(III): 1×10^{-6} mol/L, preconcentration time: 60 s
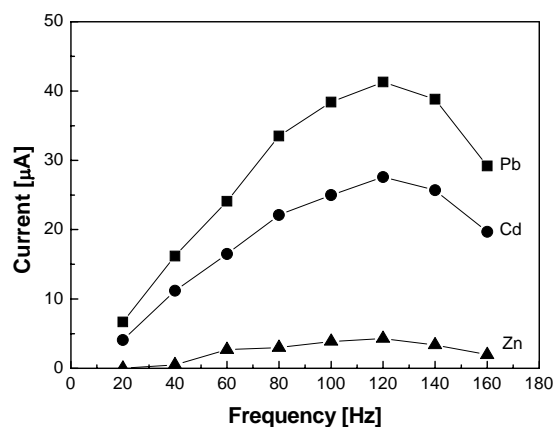

Figure 4 Dependence of current response on frequency of SWV in 0.1 mol/L acetate buffer; concentration of each of metals: 3×10^{-7} mol/L, Bi(III): 1×10^{-6} mol/L, preconcentration time: 60 s
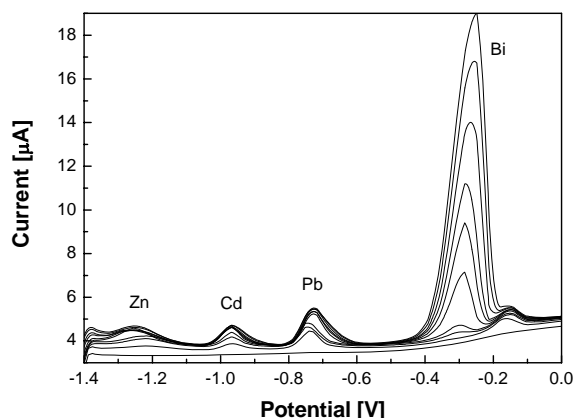
Figure 5 Square-wave stripping voltammograms (E_{step} = 12 mV, E_{pulse} = 80 mV and frequency 120 Hz). Dependence of current response of single graphite BiFE on concentration of Bi(III) (3.3 ×10^{-8} to 1 ×10^{-6} mol/L) in 0.1 mol/L acetate buffer (pH 4); concentration of each of metals: 1×10^{-8} mol/L, preconcentration time: 120 s

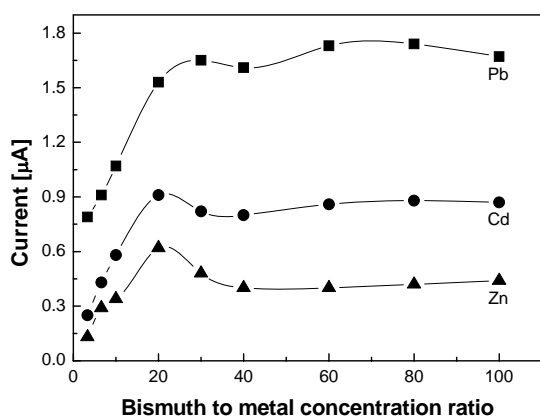*Figure 6 Dependence of current response of single graphite BiFE on concentration ratio of Bi(III) to metals in 0.1 mol/L acetate buffer (pH 4)*

Generally, the concentration of Bi(III) in the solution controls the thickness of the bismuth film. Since bismuth-metal alloying occurs mainly on the surface, without any diffusion of the metals into the bismuth film, an increase of the bismuth film thickness should have a little effect on metal stripping. The dependence of the stripping response on Bi(III) concentration at low bismuth-to-metals ratios (< 20) and low target metal concentrations (1×10^{-8} mol/L) is probably a special feature of *in-situ* prepared electrodes. We suppose that under these conditions the surface of graphite electrode is not covered by bismuth completely.

To improve the electroanalytical performance (especially the sensitivity) of the *in-situ* bismuth electrode, the preconcentration time should be optimized for the stripping responses not to be influenced by saturation. The effect of the preconcentration time was studied with the pencil-lead graphite electrode in the range from 60 to 600 s for a solution with concentration 1×10–7 mol/L of each of target metals and 1×10–6 mol/L Bi(III) in 0.1 mol/L acetate buffer. The peak heights increased linearly with time up to 360 s (Fig. 7). At a longer preconcentration time the peak heights deviate from linearity due to surface saturation.
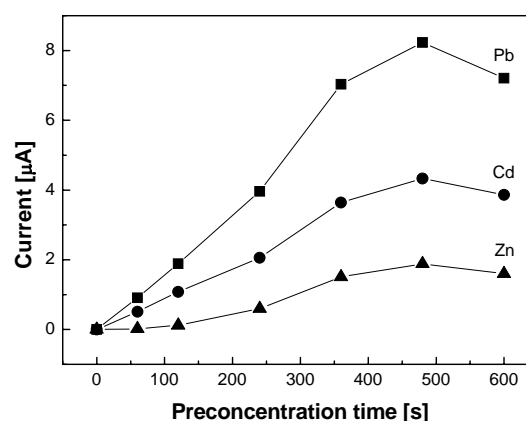

Figure 7 Dependence of current response of single graphite BiFE on preconcentration time in 0.1 mol/L acetate buffer (pH 4); concentration of each of metals: 1×10^{-7} mol/L, Bi(III): 1×10^{-6} mol/L

The ability of using the BiFE for simultaneous determination of Pb(II), Cd(II) and Zn(II) is illustrated with optimized SWV parameters in Fig. 8. All the peaks are well resolved and increase linearly with the metal concentration in the range from 1×10–8 to 1.2×10^{-7} mol/L. The resulting calibration plots were used for estimating the detection limits. On the basis of criteria for calculation of the detection limit (Y intercept + 3×SD) the detection limits were estimated as 2.4×10^{-9} mol/L for Pb(II), 2.9×10^{-9} mol/L for Cd(II) and 1.2×10^{-8} mol/L for Zn(II). In addition, one of the features of BiFE is good precision. A series of 10 repetitive measurements of a solution with concentration 1×10^{-8} mol/L of each of Pb(II), Cd(II) and Zn(II) and 2×10^{-7} mol/L Bi(III) at 120 s preconcentration time gave highly reproducible stripping peaks with relative standard deviations 4.5 % for Pb(II), 3.4 % for Cd(II) and 2.7 % for Zn(II). Good precision is attributed to the reproducible bismuth film (2.8 %).
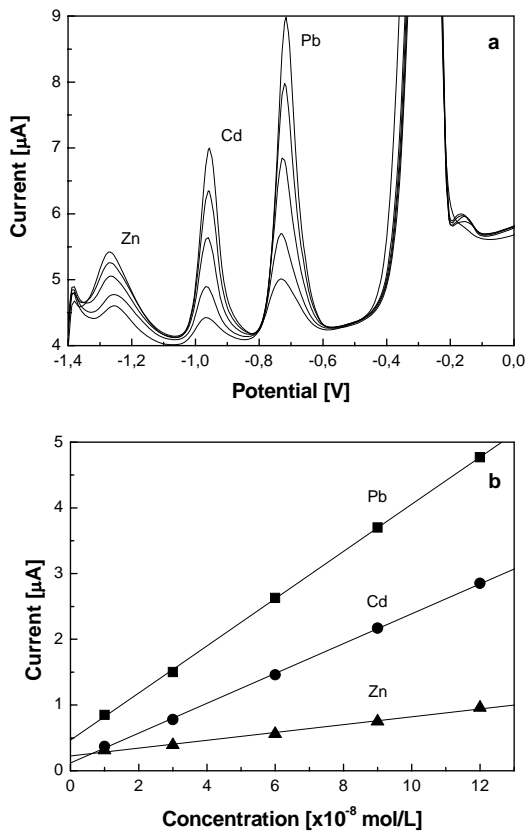
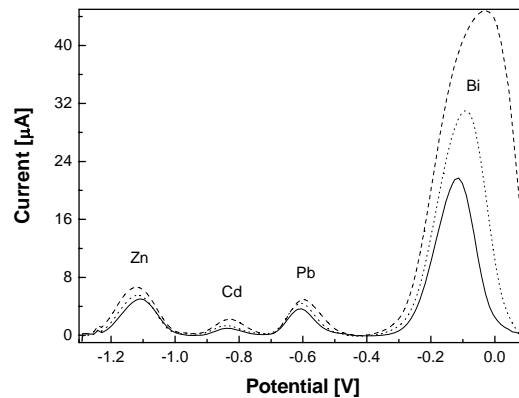concentrations than 1×10^{-6} mol/L and, moreover, the bismuth peak shape was deformed.

Figure 9 Dependence of current response of nitrogen doped DLC BiFE on concentration of Bi(III) (1×10^{-6}, 2×10^{-6}, 5×10^{-6} mol/L) for concentration of metals (6×10^{-8} mol/L) in 0.1 mol/L acetate buffer (pH 4.5)

Figure 8 Square-wave stripping voltammograms (E_{step} = 12 mV, E_{pulse} = 80 mV and frequency 120 Hz). Dependence of current response of single graphite BiFE on concentration of metals from 1×10^{-8} to 1.2×10^{-7} mol/L of each; Bi(III): 2×10^{-7} mol/L, preconcentration time: 120 s (a) and calibration curves (b)

3.2. Nitrogen-doped DLC support for bismuth film electrodes

Excellent performance of ASV with the bismuth film electrodes in determination of Pb(II), Cd(II) and Zn(II) on various carbon substrates have been already demonstrated [4, 12, 17, 25, 26].

Bismuth-plated nitrogen-doped DLC electrodes for *in-situ* determination of Pb(II), Cd(II) and Zn(II) were prepared by co-deposition of Bi(III), Pb(II), Cd(II and Zn (II) at −1.3 V vs. Ag/AgCl/Cl⁻ in a plating solution of $Bi(NO_3)_3$ in a supporting electrolyte with different contents of target metals. Stripping currents from reoxidation were recorded by SWV. The influence of the concentration of the plating solution on bismuth film formation for *in-situ* technique was investigated in the range from 1×10^{-6} to 5×10^{-6}mol/L Bi(III) in 0.1 mol/L acetate buffer solution (pH 4.5) (Fig. 9). For the ASV experiments, concentrations of 1×10^{-6} mol/L was chosen because the stripping current was not increased at higher

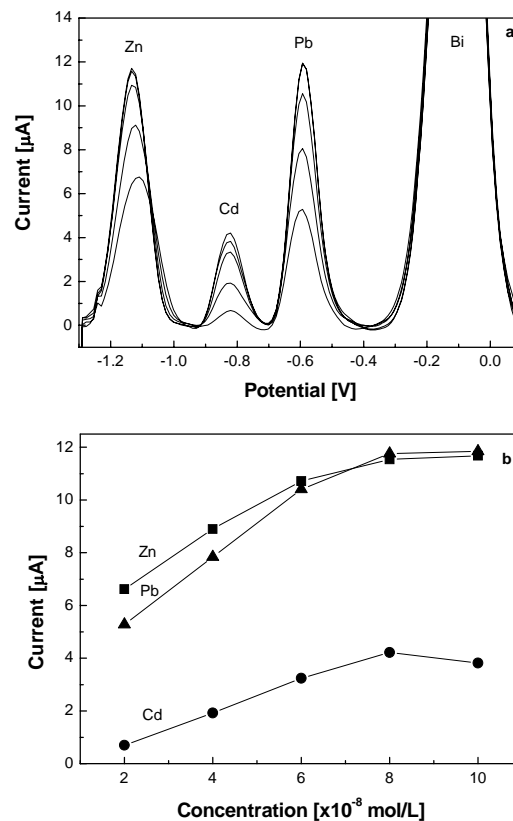*Figure 10 Square-wave stripping voltammograms (E_{step} = 12 mV, E_{pulse} = 80 mV and frequency 120 Hz). Dependence of current response of nitrogen doped BiFE on concentration of metals from 2×10^{-8} to 1.0×10^{-7} mol/L of each; Bi(III): 1×10^{-6} mol/L, preconcentration time: 120 s (a) and calibration curves (b)*

We have found previously a minimum effect of different supporting electrolytes (0.1 mol/L acetate (pH 4.5), nitrate (acidified by HNO_3) or perchlorate solutions) in bismuth plating procedure. No remarkable differences as regards the bismuth film structure and their cyclic voltammograms were observed. The dependence of voltammetric response of bismuth-plated nitrogen-doped DLC electrode on Pb(II), Cd(II) and Zn(II) concentration is shown in Fig. 10. The stripping current was linear in the range from 2×10^{-8} to 6×10^{-8} mol/L concentration of metals. At a higher concentration of target metals in solution has been observed saturation of signal.

Important parameters, stability, reproducibility and reliability of nitrogen-doped DLC film supports, multiple used in ASV have been evaluated. From Raman spectra we found no changes in the structure, however, the samples were used 20-times in ASV process (deposition - measuring - cleaning) (Fig. 11).
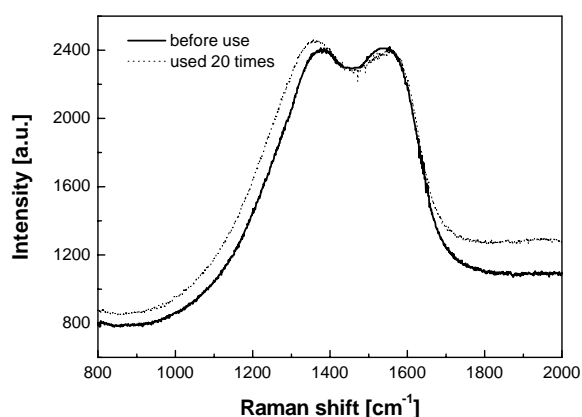

Figure 11 Raman spectra of nitrogen-doped DLC electrode before and after multiple use

4. CONCLUSION

In this work, results of heavy metals determination by anodic stripping voltammetry with bismuth film electrodes are summarized. In this field traditionally used mercury could be replaced by attractive bismuth.

A single pencil-lead graphite electrodes and high conductive silicon substrates with nitrogen-doped DLC thin films were used for determination of Pb(II), Cd(II) and Zn(II) with BiFEs.

The disc graphite BiFE was used for simultaneous *in-situ* determination of Pb(II), Cd(II) and Zn(II) by SWV in an aqueous solution. The influence of SWV parameters, Bi(III) concentration and preconcentration time was investigated. We found the optimum bismuth-to-metal concentration ratio to be 20. The dependence of the stripping responses on the concentration of target metals was linear in the range from 1×10^{-8} to 1.2×10^{-7} mol/L. Sensitivities of 35.9 µAL/µmol for Pb(II), 22.7

µAL/µmol for Cd(II) and 6.0 µAL/µmol for Zn(II) were achieved by the graphite BiFE. The detection limit was estimated as 2.4×10^{-9} mol/L for Pb(II), 2.9×10^{-9} mol/L for Cd(II) and 1.2×10^{-8} mol/L for Zn(II).

The bismuth-plated nitrogen-doped DLC electrodes were used for *in-situ* determination of target metals by SWV in an aqueous solution. The influence of the plating solution and supporting electrolyte on the stripping responses was investigated.We found that the stripping current was linear in the concentration range from 2×10^{-8} to 6×10^{-8} mol/L. At a higher concentration of target metals in solution has been observed saturation. It was found that the analytical performance of the bismuth film microelectrode array was influenced by the properties of nitrogen-doped DLC.

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