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DETERMINATION OF Cd(II) USING SQUARE WAVE ANODIC STRIPPING VOLTAMMETRY AT A CARBON PASTE ELECTRODE CONTAINING Bi-DOPED CARBON XEROGEL

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ABSTRACT. A novel carbon paste electrode (CPE) modified with Bi-doped carbon xerogel (BiCXe) is presented as a promising alternative to electrode materials used to replace mercury electrode in detection of heavy metals ions from aqueous solutions. The *ex situ* preparation of BiCXe was realized by sol-gel technique involving a reaction between a mixture of organic compounds (resorcinol, formaldehyde, glycerol formal) and a bismuth salt ($Bi(NO_3)_3 \cdot 5\ H_2O$) in the presence of a catalyst (NH_4OH), followed by gel washing, drying and pyrolysis at 550^0C/ 2h/ in inert atmosphere (Ar). Electrochemical investigation of BiCXe-CPE was performed by cyclic voltammetry (CV) and square wave voltammetry (SWV), and the detection of Cd (II) ions by square wave anodic stripping voltammetry (SWASV) in acetate buffer 0.1 M (pH = 4.5). The electroanalytical parameters of the new sensor were determined. The favourable performance of the novel electrode coupled with the mercury-free surface make this sensor very attractive for environmental monitoring of toxic Cd(II) ions.

Keywords: *carbon paste electrode; Bi-doped carbon xerogel; Cd(II) detection; square wave voltammetry; anodic stripping;*

INTRODUCTION

Detection of heavy metal ions is of big importance, due to their toxicity, their negative impact on ecological quality and their increased presence in the environment. Among the electrodes used for electrochemical detection of heavy metals ions, mercury electrode is the transducer most used, showing the best sensitivity, selectivity and reproducibility due to its regenerative active area [1].

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However, due to its high toxicity, volatility, the difficulty of handling and miniaturization, the increased purchase price and maintenance, considerable efforts have been made in the last years to replace it with other electrode materials which overcome all these shortcomings, without significant decrease in their electrochemical and sensory properties.

Carbon xerogels (CXe) are microporous carbon materials that have received considerable attention in the literature over the past decade [2–5]. These materials can be produced in different forms (as powders, thin-films, cylinders, spheres, discs, or can be custom shaped) [5]. The most important properties of these materials are their high porosity, controllable surface area and controlled pore size distribution, low electrical resistivity and good thermal and mechanical properties. These properties make them promising materials for several potential applications as electrode material for double layer capacitors or supercapacitors [6], adsorption materials for gas separation [7], catalyst supports [8], column packing materials for chromatography [9], biotechnology [10] and sensing devices [11].

Recently, carbon xerogels containing Bi (BiCXe) have been shown to offer comparable performances to Hg electrodes in detection of heavy metal ions from aqueous solutions [2]. There were reported several methods to develop Bi containing electrodes. They are using: (i) bismuth nano-powders [4]; (ii) bismuth-modified boron doped diamond [12]; (iii) *in situ* bismuth-modified multi-walled carbon nanotubes doped carbon paste [13]; (iv) bismuth-films deposited on different substrates [14-17]; (v) screen-printed electrodes modified with Bi-nanoparticles [3, 18] or Bi films [19].

In this context, the present research aims to investigate a novel electrode material based on Bi-doped carbon xerogel incorporated in carbon paste as a promising alternative to mercury electrode in detection of Cd(II) ions from aqueous solutions. The proposed electrode material was tested for determination of Cd(II) at trace level by using square wave anodic stripping voltammetry (SWASV).

RESULTS AND DISCUSSION

Electrochemical behavior of BiCXe-CPE

The favourable electrochemical characteristics of the new electrode are revealed in figure 1, which shows a comparison between CV and SWV obtained at the BiCXe-CPE and CXe-CPE. SWV is more frequently used, because is a sensitive method that can feel any noise, impurities, surface contamination, etc. which may affect the sensitivity and reproducibility of Bi electrode. To determine the optimum parameters of measurements for the proposed material, some preliminary experiments, using CV and SWV, in buffer solutions were carried out.

Acetate buffer (pH 4.5) was selected as working electrolyte for all experiments due to the fact that it is commonly used by many researchers [20-24], especially in the environmental analysis, as buffer solution for electrochemical measurements that include materials containing Bi, because the response of bismuth is more clearly defined and the oxidation occurs more easily than in other solutions.

In figure 1A are presented the cyclic voltammograms recorded for CXe-CPE and BiCXe-CPE electrodes. The redox process corresponding to Bi oxidation/reduction can be observed on the solid line voltammogram, proving its presence in the carbon paste, respectively in the BiCXe sample. The redox behavior of the BiCXe-CPE is a quasi-reversible process placed at -0.05 V *vs.* Ag/AgCl,KCl_{sat} (oxidation) and respectively at -0.58 V *vs.* Ag/AgCl, KCl_{sat} (reduction), with a peak separation (ΔE, defined as difference between anodic ad cathodic peak potentials) of 0.53 V.

A similar redox behaviour of BiCXe-CPE is observed in SWV, where the anodic oxidation can be much better observed, and the Bi oxidation peak is placed at –0.12 V *vs.* Ag/AgCl,KCl_{sat}, (figure 1B).

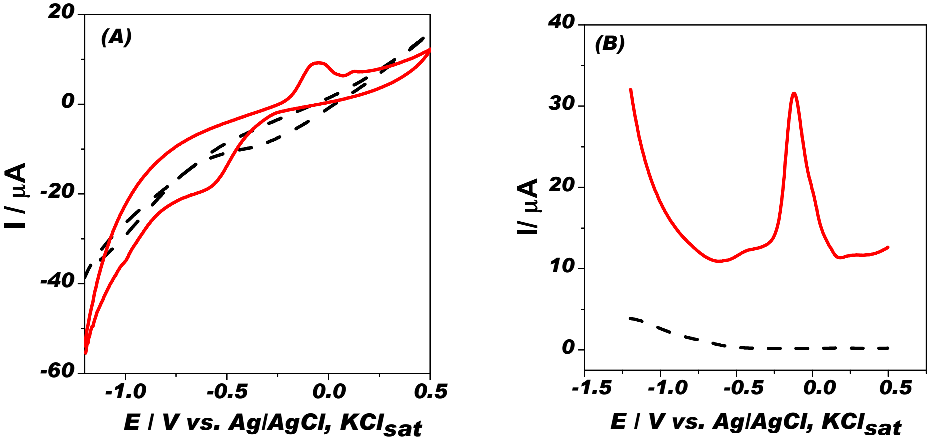

Figure 1. Cyclic (A) and square wave (B) voltammograms for CXe-CPE (dash line) and BiCXe-CPE (solid line). Experimental conditions: electrolyte, 0.1 M acetate buffer (pH 4.5); frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.004 V; starting potential, -1.2 V; equilibration, 10 s without stirring.

In the case of SWV, several frequencies and signal amplitudes were tried in order to get a well-defined answer of the modified carbon paste electrode. It was found out that the optimal frequencies domain is relatively limited. The best response of electrode was recorded between 25-50 Hz (Figure 2), so all further experiments were carried out by using a frequency of 25 Hz.

When the optimal experimental parameters were used, the recorded stripping voltammogram at BiCXe-CPE (solid-line, Figure 1B), shows a clean and undistorted stripping signal.

These results prove clearly that the investigated material contains bismuth. In the same time, it was established that the peak height is proportional to the Bi content in the carbon paste and, respectively, in the xerogel (results not shown).

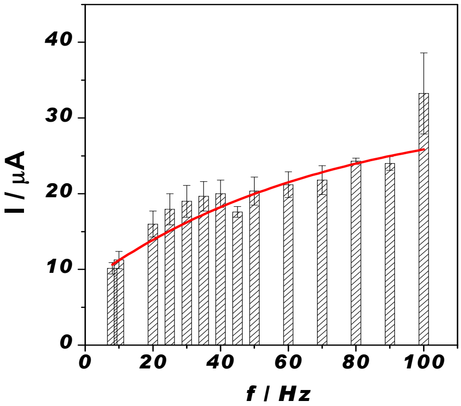

Figure 2. Influence of input signal frequency on the electrochemical response of BiCXe-CPE. Experimental conditions: electrolyte solution, 0.1 M acetate buffer (pH 4.5); frequencies, 8 - 100 Hz; amplitude, 0.05 V; scan rate, 0.004 V; starting potential, -1.2 V; equilibration time, 10 s.

To determine the stability of BiCXe-CPE, the electrode was exposed to a set of four-five successive measurements, in pure 0.1 M acetate buffer (pH 4.5) and SWV were recorded for each experiment (results not shown). There were no significant differences between the responses of the electrode, which indicates good short-time stability.

Detection of Cd(II) at BiCXe-CPE electrodes

The BiCXe-CPE electrode was further examined by recording SWASVs in the presence of Cd(II) ions (figure 3). The voltammogram exhibited a well-defined, sharp and undistorted stripping signal for Cd(II) and Bi(III) with peak potentials placed at -0.750 V and -0.12 V *vs.* Ag/AgCl, KCl_{sat}, respectively, values in agreement with those reported in the literature [25]. With the increasing of Cd(II) concentration to 20 μM, the potential of Cd(II) and Bi(III) is shifted to much positive values, *i.e.* at -0.665 V (ΔE = 0.085 V) and -0.063 V *vs.* Ag/AgCl, KCl_{sat} (ΔE = 0.039 V), respectively.

Optimisation of anodic stripping voltammetry conditions for Cd(II) detection was studied. Thus, the influence of the deposition time on the 2 μM Cd(II) ion detection was investigated in the range of 30-360 s. In the inset of figure 3 a linear dependence was observed with a slope of 1.6 $10^{-2} \pm 0.02\ 10^{-2}$ μA/s (R = 0.9994, n = 7). Consequently, a deposition time of 120 s was chosen for further measurements as a compromise between sensibility and experiment duration.

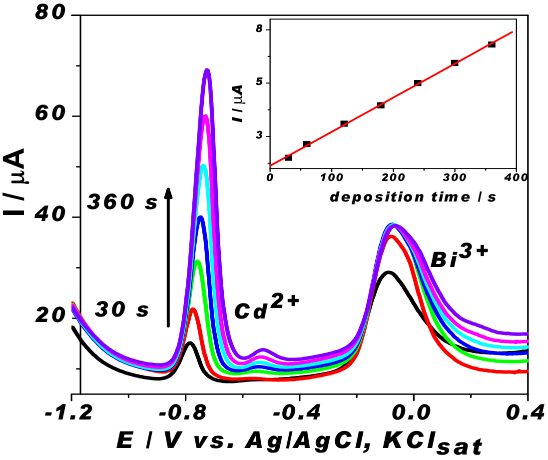

Figure 3. SWASVs of 2 μM Cd (II) at BiCXe-CPE electrode for different deposition time. Inset Cd(II) peak current *vs*. deposition time dependence. Experimental conditions: electrolyte, 0.1 M acetate buffer (pH 4.5); frequency, 25 Hz; amplitude, 0.05 V; step potential, 0.004 V; starting potential, -1.2 V; deposition potential -1.2 V; deposition time, 30 s to 360s under continuous stirring at 500 rpm; equilibration, 10 s without stirring; electrode conditioning, +0.3 V; duration, 30 s under continuous stirring at 500 rpm.

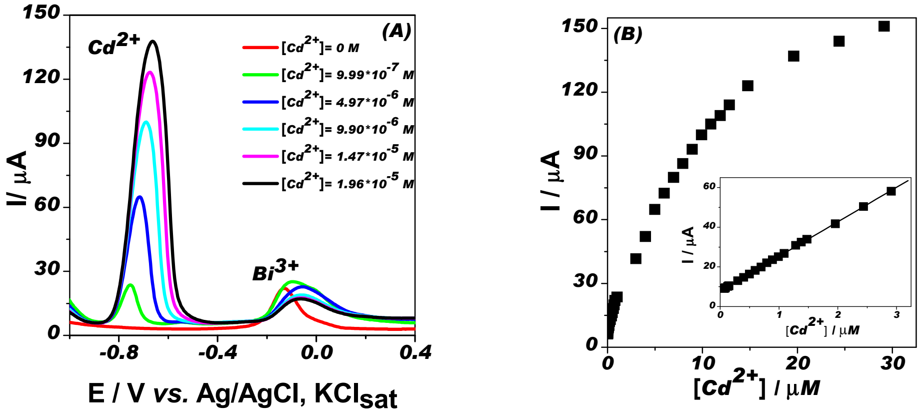

Figure 4. SWASVs recorded on BiXe-CPE for Cd(II) ion detection (A) and corresponding calibration curve (B). Experimental conditions: see Figure 3.

The detection of Cd(II) ions by recording SWASVs in the range of 0-30 µM Cd(II) lead to the obtaining of a corresponding calibration curve (figure 4B). The linear domain is in the range of 0 - 3 µM Cd(II) (figure 4B inset) with a slope of 17.39 ± 0.07 A/M (R = 0.99983, n = 21 points). The detection limit (LOD) was 0.045 µM/L (or 5 µg/L) (signal/noise = 3) The LOD value is in concordance with the maximum contaminant level goals for Cd concentration in drinking water requested by the EU and USA legislations [26-27].

One of the most important performance characteristic of the sensor is its reproducibility, expressed as relative standard deviation (RSD) of the peak current or of the peak potential (results not shown). In the case of three successive measurements of 2 µM Cd(II) at BiCXe-CPE in 0.1 M acetate buffer pH 4.5, the mean peak intensity is 2.66 10^{-5} ± 8.38 10^{-8} A, with a RSD of 0.31% and the mean peak potential is -0.753 ± 0.006 V *vs.* Ag/AgCl, KCl_{sat}, with a RSD of 0.8%, respectively. The obtained RSD values indicate a good reproducibility of the obtained sensor, recommending the BiCXe-CPE as a good sensor for Cd(II) detection.

Interference of Pb(II) to Cd(II) detection at BiCXe-CPE electrodes

In order to investigate the possible interference with other heavy metals, SWASVs were recorded in solution containing a mixture of Cd(II) and Pb(II) of same concentrations. In figure 5 it is observed that well-defined peaks attributed to the oxidation of Cd(II), Pb(II) and Bi(III), are placed at -0.766 V, -0.52 V and -0.03 V *vs.* Ag/AgCl,KCl_{sat}, respectively. Even if a shift of oxidation potential is observed when the ions concentration is increasing, the peak separation is enough large to avoid interferences in both Cd(II) or Pb(II) detection in a mixture sample.

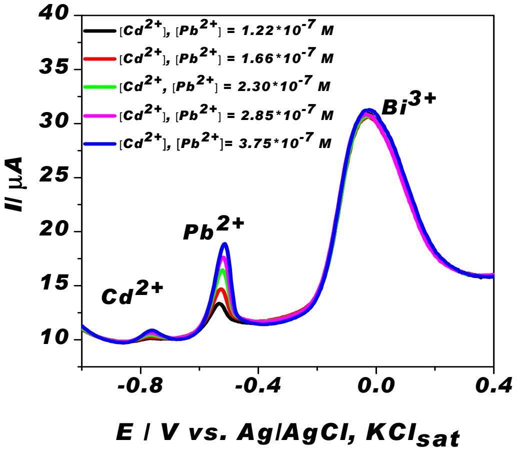

Figure 5. SWASVs responses for increasing concentrations of Cd(II) an Pb(II) at BiCXe-CPE electrode. Experimental conditions: starting potential, -1.3 V *vs.* Ag/AgCl, KCl_{sat}; other conditions see figure 3.

CONCLUSIONS

The BiCXe-CPE electrode successfully exploits the favourable mechanical and electrochemical properties of carbon paste electrodes and combines them with the unique electroanalytical characteristics of Bi-based xerogels.

The modification of carbon paste electrodes with carbon xerogels containing Bi could be used for the sensitive detection of Cd(II) ions, without interfering with Pb detection.

The low cost of graphite, simplicity of fabrication of the BiCXe-CPE electrodes and the obtained detection limit recommend this electrode for replacing mercury electrode in the detection of Cd(II) ions from aqueous solutions.

EXPERIMENTAL

Materials

Chemicals for *ex situ* preparation of Bi-doped carbon xerogel (BiCXe) involve $Bi(NO_3)_3 \cdot 5\ H_2O$ (Alfa Aesar- UK), glycerol formal (Sigma Aldrich), resorcinol - $C_6H_6O_2$, formaldehyde, catalyst NH_4OH, glacial acetic acid (the last three from MERCK, Germany) and $Cd(NO_3)_2$, Pb $(CH_3COO)_2$ (Reactivul Bucuresti). For carbon paste electrode preparation, graphite powder and paraffin oil from Fluka Sigma-Aldrich, Germany were used. Acetate buffer (0.1 M, pH 4.5) used in SWV experiments was prepared by mixing 0.2 M NaAc (Reactivul Bucuresti, Romania) solution with 0.2 M HAc solution. Cd (II) and Pb(II) 10^{-6} M stock solutions were prepared by dissolving appropriate amounts of Cd $(NO_3)_2 \cdot 4\ H_2O$ and Pb $(CH_3COO)_2 \cdot 3\ H_2O$ into the buffer solution (pH 4.5). All solutions were prepared with double distilled water.

Apparatus and methods

Cyclic and square wave voltammetry (SWV, SWASV) were performed with an AUTOLAB PGSTAT 12/100, Booster 20A, µAutolab type III/ FRA2, electrochemical station. A pH-meter, MV 870 DIGITAL-pH-MESSAGERÄT-PRACITRONIC, was used to measure the pH of solutions. A conventional three-electrode system consisting of a BiCXe-CPE with inner diameter of 2 mm, a counter electrode made of platinum, and an $Ag/AgCl/KCl_{sat}$ reference electrode were used for electrochemical measurements.

Procedures

Synthesis of BiCXe

The obtaining of the carbon xerogels through sol-gel synthesis consisted in several steps [2]:

- ✓**sol preparation**: based on the poly-condensation reaction of resorcinol (R) with formaldehyde (F) in basic catalysis of NH_4OH in the presence of glycerol formal / acetic acid containing Bi salt;
- ✓**gel aging or gelation** in aging-oven;
- ✓**gel washing**: in acetic acid;
- ✓**drying** in ambient conditions;
- ✓**thermal treatment**: pyrolysis (550^0C/ 2h/ Ar)

The BET analysis revealed that the xerogels have a specific surface area of 80 m^2g^{-1} and a specific pore volume of 0.04 cm^3g^{-1}, suggesting that their structure presents mesopores. In the same time, it was found that Bi did not affect the porosity of the carbon xerogel.

Preparation of the carbon paste electrode containing Bi doped carbon xerogel (BiCXe-CPE)

CXe-CPE (blank) and CXe doped with bismuth-CPE (BiCXe-CPE) electrodes were prepared as follows: graphite powder (0.02 g), CXe or BiCXe (0.04 g) and paraffin oil (30 μL) were carefully mixed in a mortar and then homogenized by continuous hand-mixing for 30 min. (Figure 6, step a). The paste was then introduced in a cylindrical holder (Figure 6, step b) and the electrode surface was smoothed by polishing on a normal clean white paper. The electrode was ready to use, without any further chemical or electrochemical pretreatment. This step was repeated by replacing the used paste with a fresh one before each experiment.

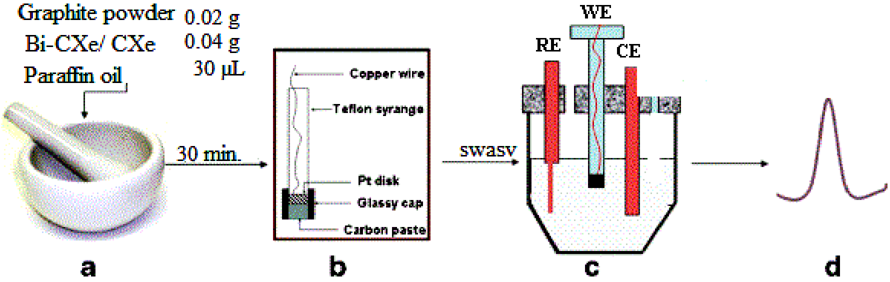

Figure 6. Preparation and characterization of the carbon paste electrode containing xerogels

Electrochemical characterization of the carbon paste electrode containing BiCXe

The working electrode was installed in a conventional electrochemical cell filled with 10 mL acetate buffer 0.1 M, pH = 4.5 (Figure 6, step c) and connected to a potentiostat. Before each experiment, the surface of electrode was renewed and polished on a white paper sheet.

The electrochemical measurements were performed by applying the desired potential to the electrodes and measuring the generated current during the potential scan. The SWV voltammograms were recorded after applying 10 s equilibration period, stage followed by application of a positive- going square wave voltammetric potential scan from -1.2 to 0.5 V *vs.* Ag/AgCl,KCl$_{sat,}$ with a frequency of 25 Hz, pulse amplitude of 0.05 mV, and step increment of 4 mV. These parameters were fixed after a systematic investigation of the electrochemical process. All the experiments were carried out at room temperature.

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REFERENCES

[1]. J. Wang, *Electroanalysis*, **2005**, *17*, 1341.
[2]. M. Gich, C. Fernandez-Sanchez, L.C. Cotet, P. Niu, A. Roig, *Journal of Materials Chemistry.* A, **2013**, *1*, 11410.
[3]. I. Svancara, C. Prior, S.B. Hocevar, J. Wang, *Electroanalysis*, **2010**, *22(13)*, 1405.
[4]. G. Aragay, *Electrochimica Acta*, **2012**, *84*, 49.
[5]. J.A. Rodrigues, C.M. Rodrigues, P.J. Almeida, I.M. Goncalves, R.G. Comptonb, A.A. Barros, *Analytica Chimica Acta*, **2011**, *701*, 152.
[6]. J. Lee, S. Yoon, T. Hyeon, S.M. Oh, K.B. Kim, *Chemical Comunication*, **1999**, 2177.
[7]. A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar*, Journal of Hazardous Materials B*, **2005**, *122*, 161.
[8]. T.W. Kim, P.W. Chung, I.I. Slowing, M. Tsunoda, E.S. Yeung, V.S.Y. Lin, *Nano Letters 8*, **2008**, *11*, 3724.
[9]. M. Steinhart, C. Liang, G.W. Lynn, U. Gösele, S. Dai, *Chemestry of Materials,* **2007**, *19 (10)*, 2383.
[10]. C. Liang, S. Dai, G.A. Guiochon, *Analytical Chemistry,* **2003**, *75*, 4904.
[11]. C.-S. Chu, Y.-L. Lo, *Sensors and Actuators B*, **2008**, *129*, 120.
[12]. Toghill K. E., G.G. Wildgose, A. Moshar, C. Mulcahy, R.G. Compton, *Electroanalysis,* **2008**, *20*, 1731.
[13]. J. Hua Luo, X. Xia Jiao, N. Bing Li, H. Qun Luo, *Journal of Electroanalytical* Chemistry, **2013**, *689*, 130.

[14]. D. Martín-Yerga, M. Begoña González-García, A. Costa-García-Nanobioanalysis Group, *Talanta*, **2013**, *116*, 1091.

[15]. A, Charalambous, A. Economou, *Analytica Chimica Acta*, **2005**, *547*, 53.

[16]. H. Xu, L. Zeng, D. Huang, Y. Xian, L. Jin, *Food Chemistry*, **2008**, *109*, 834.

[17]. Y. Wu, N. Bing, H.Q. Luoa, *Sensors and Actuators B: Chemical,* **2008**, *133*, 677.

[18]. J.C. Quintana, F. Arduini, A. Amine, F. Punzo, G. Li Destri, C. Bianchini, D. Zane, A. Curuli, G. Palleschi, D. Moscone, *Analytica Chimica Acta*, **2011**, *707*, 171-177.

[19]. C. Kokkinos, A. Economou, I. Raptis, C. E. Efstathiou, *Electrochimica Acta*, **2008**, *53*, 5294-5299.

[20]. V. Rehacek, I. Hotovy, M. Vojs, T. Kups, L. Spiess, *Electrochimica Acta,* **2012**, 192-196.

[21]. G.D. Pierini, A.M. Granero, M.S. Di Nezio, M.E. Centurión, M.A. Zon, H. Fernández, *Microchemical Journal,* **2013**, 102–106.

[22]. Y. Tian, Lianzhe Hu, S. Han, Y. Yuan, J. Wang, G. Xu, *Analytica Chimica Acta*, **2012**, 41–44.

[23]. J. Saturno, D. Valera, H. Carrero, L. Fernandez, *Sensors and Actuators B: Chemical,* **2011**, 92–96.

[24]. H. Sopha, S.B. Hocevar, B. Pihlar, B Ogorevc, *Electrochimica Acta*, **2012**, 274–277.

[25]. S.B. Hocevar, I. Svancara, K. Vytras, B. Ogorevc, *Electrochimica Acta* **2005**, *51*, 706-710.

[26]. ***Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption; published in *Official Journal* L 330, 05/12/**1998** P. 0032 – 0054; *http://eur-lex.europa.eu/legalcontent/EN/TXT/?uri=CELEX:31998L0083* visited the 29th of September 2014.

[27]. *** US Environmental Protection Agency, *http://water.epa.gov/drink/contaminants/basicinformation/cadmium.cfm* visited the 29th of September 2014.