
Volume 1 | Number 1 | Jan 2013 | Pages 1–100
NJC
New Journal of Chemistry
www.rsc.org/njc
A journal for new directions in chemistry
ROYAL SOCIETY OF CHEMISTRY
cnrs

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Electrode modified with nanoparticles composed of 4,4'-bipyridine-silver coordination polymer for sensitive determination of Hg(II), Cu(II) and Pb(II)

Ana Chira,[a,b] Bogdan Bucur,*[a] Madalina Petruta Bucur [a] and Gabriel Lucian Radu *[a,b]

We have modified a glassy carbon electrode (GCE) with nanoparticles composed of a 4,4'-bipyridine-silver coordination polymer (CP) and showed that this CP can be applied to the sensitive differential pulse voltammetric analysis of the ions Hg(II), Cu(II) and Pb(II). The coordination polymer was prepared by mixing solution of silver nitrate and 4,4'-bipyridine at room temperature. The surface of the GCE was modified with an organic layer of synthesized 1-[(4-nitrophenyl)methyl]-4,4'-bipyridinium and silver ions which causes binding of the added Ag-bipy CP. The anodic (oxidative) peaks of the electrode are at +300 mV for Hg(II), –70 mV for Cu(II), and at –540 mV for Pb(II) [versus Ag/AgCl]. Under optimal conditions, the calibration graphs are linear in the conentration ranges from 0.2 to 10 μg L^{-1} for Hg(II), from 1.3 to 6.4 μg L^{-1} for Cu(II), and from 4.1 to 20.7 μg L^{-1} for Pb(II). The respective detection limits are 0.09 μg L^{-1} Hg (II), 0.71 μg L^{-1} Cu(II) and 2.3 μg L^{-1} Pb (II), The relative standard deviation is 3.2 % at a level of 4 μg L of Hg(II) for n=10. The modified electrode was applied to the analysis of Hg(II) in spiked fish samples, and of Cu(II), Pb(II), and Hg(II) in spiked plant samples, and recoveries range from 90 to 108%. This is the first paper that presents the use of 4,4'-bipyridine-silver coordination polymer for heavy metal electrochemical detection.

Introduction

Heavy metals such as mercury, lead and copper are toxic and their concentration in environment and food must be analyzed. Various analytical methods have been developed for heavy metals analysis with good performances, but based on complex and expensive equipments: i.e. cold vapor atomic absorption spectrometry [1], inductively coupled plasma mass spectrometry [2], gas chromatography-mass spectrometry [3], X-ray fluorescence spectrometry [4], or atomic fluorescence spectrometry [5]. Rapid, selective and inexpensive alternative analytical methods are required for metals detection at very low concentrations in environmental and food samples. Different electrochemical methods based on simpler equipments [6] have been proposed as alternative techniques. Thus, electrodes for electrochemical analysis of heavy metals have been modified with polymeric membranes [7], ion exchange resin [8], carbon nanotubes [9] or nanoparticles [10]. The development of metallic or carbon based nanoscale materials with superior electric and catalytic properties led to improved electrochemical sensors and biosensors [11]. Despite their advantages, the electrochemical methods are less aplied in routine analytical laboratories and significant improvements are still required.

Organometallic coordination polymers obtained by self-assembly via non-covalent interactions [12] are versatile materials used for molecular storage, separation, catalysis, ion exchange, etc. [13], but less investigated for electrochemical sensors development. Coordination polymers (CP) are supramolecular assemblies of metal ions (or metal clusters) and organic ligand (linkers) as units linked via coordination bonds and other chemical bonds. Such metal-ligand compounds can extend into one, two or three dimension via more or less covalent metal-ligand bonding [14]. Coordination bonds are formed by the donation of a lone electron pair of the ligand to the metal cation and electrostatic attractions between the positively charged metal ion and a negatively charged/polarized donor atom of the ligand [14]. Various supramolecular coordination polymers based on metal complexes with aromatic nitrogen-donor ligands have been produced and characterized [15]. 4,4'-bipyridine is a prototypical bridging ligand [16]. Different derivatives of 4,4'-bipyridine ligands in the self-assembly process, can form coordination polymers which may have one-dimensional, two-dimensional and three-dimensional structures with metal ions [17]. The coordination polymeric structure of bipyridine was used for modification of electrodes with application in tryptophan determination [18], electrocatalysis of oxygen reduction [19] and electrochemical performance in lithium-ion batteries [20].

We present a glassy carbon electrode modified with nanoparticles of 4,4'-bipyridine-silver coordination polymer for highly sensitive analysis of heavy metals (Hg (II), Cu (II) and Pb (II)) by differential pulse voltammetry. The coordination polymers were immobilized on the glassy carbon electrode surface via an organic layer that contains phenylmethyl-4,4'-bipyridinium [21] and coordinated silver ions. To the best of our knowledge, this is the first paper that presents the use of 4,4'-bipyridine-silver coordination polymer for heavy metal electrochemical detection. The modification method is rapid (an electrode is produced in less than 30 minutes), electrodes are stable and can be used for the analysis of at least 70 real samples.

Experimental

Reagents

1-[(4-nitrophenyl)methyl]-4,4'-bipyridinium (N-PMB) was synthesized according to a previous procedure [21, 22] by refluxing a solution containing 0.0702 g of 4,4'-bipyridine and 0.0193 g of 4-nitrobenzylchloride (4:1 molar ratio) in 45 mL of acetonitrile and water (2:1) for 22 hours. The product was analysed by HPLC-MS and stored in refrigerator for up to 3 months. All the other chemicals were bought from Sigma: mercury(II) acetate, copper(II) chloride, lead(II) acetate, silver nitrate, acetonitrile (ACN, for HPLC), sodium nitrite, potassium ferrocyanide, potassium ferricyanide, potassium phosphate monobasic, sodium phosphate dibasic, potassium chloride, sodium acetate, acetic acid. Aqueous solutions were prepared with purified water (18 MΩ cm−1, Millipore). Working standards were daily prepared by suitable dilutions from the stock solution. Phosphate buffer saline PBS (0.1 M, pH 7.0, supplemented with 0.1 M KCl) was used for electrode characterization by cyclic voltammetry and electrochemical impedance spectroscopy. Acetate buffer (0.1 M, pH 5.0, supplemented with 0.1 M KCl) was used for heavy metals detection by DPV.

Apparatus

All electrochemical measurements were carried out using a PGSTAT 302N potentiostat/galvanostat (Metrohm-Autolab) equipped with a conventional three-electrode cell and controlled using Nova 1.8 software. The working electrode was a modified glassy carbon (GCE) with a geometrical area 0.07 cm² from Metrohm, reference electrode was Ag/AgCl//3M KCl (Metrohm) and platinum foil was used as auxiliary electrode. Elemental analyses of Ag-4,4'-bipyridine coordination polymer for carbon, nitrogen and hydrogen were carried out with a Heraeus CHNO-Rapid apparatus. The crystallographic characterization of the coordination polymer was carried out with a SMART APEX CCD diffractometer (Bruker). Fourier Transform Infrared (FT-IR) spectra were recorded with a Bruker-Tensor 27 Fourier Transform spectrometer equipped with a RT-DLa TGS detector. Each measurement was recorded in transmittance (ratio sample: KBr,1:100) in the range 4000-400 cm^{-1} and average value of 96 co-added scans, 10 kHz scan rate with 4 cm^{-1} resolution and 4 mm aperture. The spectra were registered and ascribed using Opus software, version 6.0. The grids were examined using a Philips electron microscope EM 208S (acceleration voltage of 80 kV); then snapshots were taken using a video camera Veleta and the iTEM Olympus Soft Imaging System. The buffers were adjusted using an Autolab pX1000 module for pH measurements.

Synthesis of Ag-4,4'-bipyridine coordination polymer (Ag-bipy – CP)

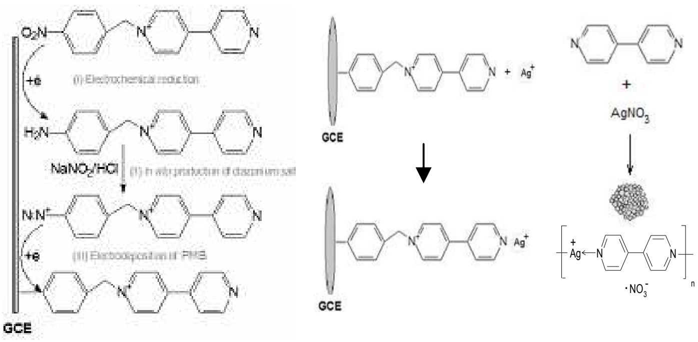
The Ag-bipy-CP was prepared as follows: 1 mL aqueous solution of 1 mM $AgNO_3$ was mixed with 1 mL of 1 mM 4,4'-bipyridine prepared in acetonitrile under stirring at room temperature and a white precipitate was formed. Ag-bipy-CP were separated by centrifugation and washed with purified water. Finally, Ag-bipy-CP was resuspended in 20 µL water and was used immediately for electrode modification. The synthesized silver nanoparticles were characterized by TEM, FT-IR and crystal structure analysis.

Deposition of Ag-bipy -CP on glassy carbon electrode (Ag-bipy-CP/PMB/GCE)

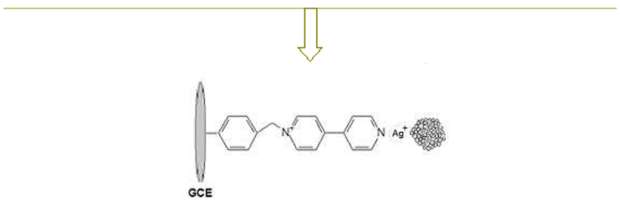
Before modification, the GCE was polished with alumina (0.3 µm, Metrohm), thoroughly rinsed with Milli-Q water and dried with argon stream. The formation of an organic layer that contains 4,4'-bipyridine on GCE surface is based on: (1) 1-[(4-nitrophenyl)methyl]-4,4'-bipyridinium reduction to N-(p-aminobenzyl)-4,4'-bipyridine at -0.6 V for 600 s by chronoamperometry, (2) transformation *in situ* of amino groups into diazonium in presence of $NaNO_2$ and (3) electrochemical reduction of diazonium groups at -0.25 µA for 60 s by chronopotentiometry [21, 22]. The GCE electrochemical covered by a phenylmethyl-4,4'-bipyridinium (PMB) layer was immersed in a solution of 1 mM $AgNO_3$ for 10 minutes. GCE were washed with water, dried in argon stream and, in the last step, 5 µL of freshly prepared Ag-bipy-CP was deposited on the modified electrode surfaces. Finally, Ag-bipy-CP/PMB/GCE was washed with water and dried with argon stream. The fabrication process of the modified electrode is presented in Fig. 1.

Ag-bipy-CP/PMB/GCE surface characterization

The modification of the electrodes was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV was made in a solution of 1 mM potassium ferricyanide in PBS at 0.1 V s^{-1} scan rate, from 0.6 V to –0.2 V. The EIS measurements were made in PBS containing 1 mM ferri/ferrocyanide in equimolar ratio at open circuit potential. An alternative potential with amplitude of 5 mV (rms) was applied at 40 frequencies logarithmically distributed between 9.5 kHz and 0.1 Hz frequency range. After each modification step, the electrochemical behavior of the electrode surface was investigated by CV and EIS. The results were represented as Nyquist plots and interpolated using Randles equivalent circuit. The charge transfer resistance (R_{ct}) was used for the surface characterization.



PMB-GCE (A) Ag/PMB/GCE (B) Ag-dipy-CP (C)



Ag-dipy-CP/PMB/GCE (D)

Figure 1. Schematic representation of the GCE surface modification. (A) PMB electrodeposition on the GCE surface (PMB-GCE); (B) PMB/GCE immersion in $AgNO_3$ (Ag/PMB/GCE); (C) 4,4'-dipyridine-silver coordination polymer formation (Ag-dipy-CP); (D) Modified electrode (Ag-dipy-CP/PMB/GCE)

Hg (II), Cu (II) and Pb (II) Analysis

Heavy metals were analyzed by differential pulse voltammetry (DPV). A preconditioning of the Ag-bipy-CP/PMB/GCE surface was carried out before each analysis by recording ten cyclic voltammograms from −0.2 to +0.6 V at a scan rate of 100 mV s^{-1} in electrolyte solution (acetate buffer pH 5). The Ag-bipy-CP/PMB/GCE was immersed in 25 mL magnetically stirred standard solution or sample and Me (II) were reduced to Me (0) by applying a potential of −0.6 V for 300 s. Then, the electrode was rinsed with distilled water and transferred to another cell that contained of 25 mL deoxygenated acetate buffer. The Hg (II), Cu (II) and Pb (II) analysis was carried out by DPV from -0.65 to 0.55 V with 10 mV s^{-1} scan rate; 25 mV modulation amplitude; 50 ms modulation time and 5 mV step potential. If only Hg (II) was analyzed then the DPV was carried out from 0 to 0.5 V and the electrolyte solution was not deoxygenated. Electrode regeneration was performed by removing the analytes at a potential 0.8 V for 100 s in stirred acetate buffer. All electrochemical experiments were carried out at ambient temperature. One Ag-bipy-CP/PMB/GCE can be used at least 70 times and we did not observed any unspecific adsorption on the surface.

Real samples preparation

The frozen cod and tuna fish samples were purchased from a local supermarket. The fish samples were thawed at room temperature and then water excess was removed by filter paper. The samples were digested according to a procedure [23]: 2 g of fish was placed in a digestion vessel and 5 mL HNO_3 (fuming 100%), 2.5 mL H_2SO_4 (98%) and 1 mL HCl (37%) were added. The vessel was immediately covered and after 20 minutes was placed in the water bath at 100 ˚C for 1 hour. In the residual solution was diluted to 50 mL with distilled water. Then, 3 mL of this solution was diluted to 10 mL of 0.05 M HCl buffered at pH 5 and analyzed by DPV.

The folk medicinal plant samples (*Alchemilla vulgaris, Galium verum, Hypericum perforatum,* and *Verbascum densiflorum*) were purchased, dried and crushed from a local herbal store. Each sample of the dried plant materials was mineralized in a mixture of concentrated nitric acid (HNO_3) and perchloric acid ($HClO_4$), [3:2 v/v]. Thus, 1 g of sample was added to 5 mL of a mixture of acids (HNO3: HClO4 = 3: 2), then the samples were heated at 100 °C for 3 hours to evaporate the acids. Then, 5 mL 1 M HCl was added to the mineralized sample and the resulting mixture was heated until a clear solution was obtained (~ 1 h) [24]. The resulting solution was filtered, buffered at pH 5 and analyzed by DPV.

Results and discussion

The modified electrodes developed for heavy metals detection were produced by electrodeposition of a phenylmethyl-4,4'-bipyridinium layer using diazonium chemistry followed by binding of nanoparticles of Ag-bipy conducting polymer via coordination bonds. The Ag-bipy-CP nanoparticles were prepared from $AgNO_3$ and 4,4'-bipyridine and characterized by elemental analysis, X-ray crystallography, FT-IR and TEM.

Characterization of Ag-bipy-CP nanoparticles

The elemental analysis for carbon, nitrogen and hydrogen of the synthesized Ag (I) coordination polymers indicated a composition of C: 37.29 %, H: 2.54 % and N: 12.86 % that is similar with the theoretical composition of a chain $\{[Ag(bpy)]NO_3\}_n$ polymer: C: 36.84%, H: 2.47% and N: 12.88%. The coordination polymer has an open framework supermolecular structure that was verified from the crystallographic X-ray data (Figure S-1) [25].

The comparison of IR spectra of 4,4'-bipyridine and Ag-bipy-CP (fig. S-2) shows that the absorption bands recorded for the coordination polymer are shifted to higher frequencies as a result of coordination. Absorption bands attributed to CH aromatic nucleus were more displaced (about 20 cm^{-1}), probably due to modification of the electronic density of the aromatic ring. The displacement towards higher frequencies of the absorption band at 1595 cm^{-1}, specific stretching vibration of the C = N and C = C from 4,4'-bipyridine indicate that it is coordinated with bridge to the metal ion. Also, the absorption band at 608 cm^{-1}, attributed to bending vibrations in plan of pyridine rings was shifted to 20-30 cm^{-1} towards higher frequencies and was turned into a doublet due to the rotation of aromatic ring around C-C bridge [26]. The shifting of absorption band at 810 cm^{-1} attributed to the aromatic ring is due to the involvement of coordinated 4,4'-bipyridine in hydrogen bridges. Another band characteristic for coordinated 4,4'-bipyridine at 1222 cm^{-1} is due to deformation vibration in plan of the C-H bond. The most intense band in the FT-IR spectrum is the absorption band at 1384 cm^{-1} which corresponds to stretching vibrations of the nitrate groups.

Fig. S-3 shows the TEM image of the coordination polymer formed. They consist of 2-D thin planar structures with side length less than one micrometer.

Characterization of the Ag-bipy-CP/PMB/GCE

The different steps of the GCE modification process were characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) (Fig. 2). The CV of ferricyanide recorded for GCE covered by a PMB layer shows a partial fouling of the electrode surface. The adsorption of silver ions on PMB-GCE leads to an increase of CV peaks. We attribute this observed increase to the positive charge of the Ag (I) ions that attract ferrocyanide/ferricyanide anions towards the electrode surface. The deposition of 5 μL Ag-bipy-CP increased once again the peaks intensity due to a higher surface area and positive electrostatic charge. For 10 μL Ag-bipy-Cp deposition the electrode surface was passivated and electroactive $Fe(CN)_6^{3-}$ ions have difficult access to the electrode surfaces through the blocking CP. The procedure of obtaining modified electrodes was achieved in about 30 minutes.

The Ag-bipy-CP deposited on the GCE is electrochemically active and remain stable after cycling. Even after 10 cycles recorded in the domain of 0.6 to –0.8 V GCE modified electrode did not change the electrochemical characteristics. The Ag-bipy-CP/PMB/GCE was stored in PBS and is stable for at least 10 days.

Electrochemical properties of the modified electrode were studied by EIS (Fig. 2). The variation of the R_{ct} values reflects the modifications of the peaks intensity previously described for the characterization by CV. For a bare GCE it was obtained a R_{ct} of 0.358 kΩ that is substantially increased to 7.26 kΩ by electrodeposition of PMB layer a result that indicate a partial surface fouling. Both the immersion of PMB-GCE in $AgNO_3$ and deposition of Ag-bipy-CP lead to a decrease of R_{ct} to 6.16 kΩ and 4.31 kΩ, respectively (table S-1).

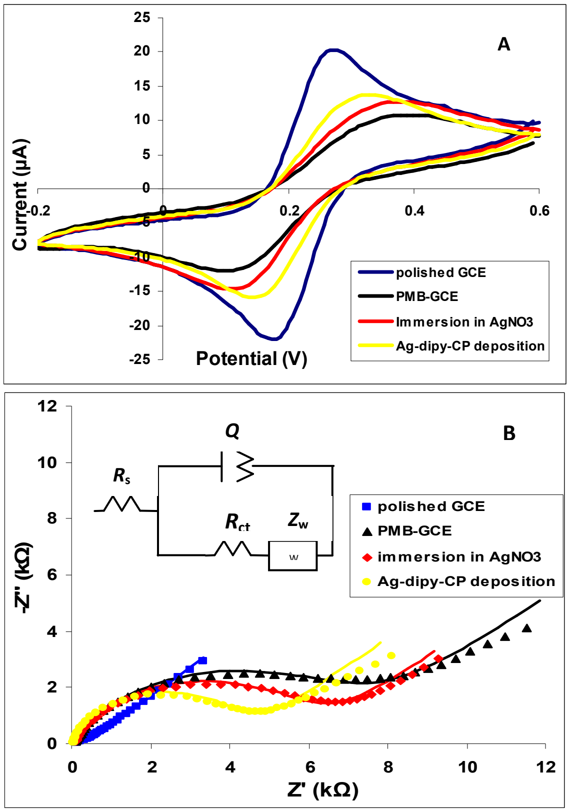


Figure 2. Characterization of different modification steps by CV (A) and EIS (B) recorded after each step of electrode modification: bare GCE (blue); PMB electrodeposition (black); immersion in $AgNO_3$ (red); Ag-dipy-CP deposition (yellow). Points are the experimental data and the lines are the fitted curves obtained using the equivalent circuit. Insert: Randels equivalent circuit used for EIS data fitting.

The chelation of the Ag^+ ions with the bipyridine form PMB/GCE surface confers high conductivity of the modified electrode and led to successful covalent immobilization of the Ag-bipy-CP. We have observed that Ag-bipy-CP improve the electron transfer toward ferrocyanide/ferricyanide. Thus, R_{ct} was smaller for Ag-bipy-CP/PMB/GCE in comparison with Ag/PMB/GCE that was already lower than PMB/GCE.

Optimization of metal ions determination

The preconcentration time, reduction potential and pH were investigated to determine the optimum conditions for the analysis of Hg (II) ions with the developed Ag-bipy-CP/PMB/GCE. The analysis involves three steps: preconcentration of metal ions, reduction at fixed potential and oxidation by DPV:

Preconcentration step:

Ag-bipy-CP/PMB/GCE + Me(II) (solution) → Ag-bipy-CP/PMB/GCE Me(II)(surface)

Reduction step:

Ag-bipy-CP/PMB/GCE Me(II) (surface) + $2e^-$ → Ag-bipy-CP/PMB/GCE Me(0)(surface)

Oxidation step:

Ag-bipy-CP/PMB/GCE Me(0) (surface) → Ag-bipy-CP/PMB/GCE + Me(II) (solution) + $2e^-$

The modified electrode was immersed in 1 μg L^{-1} Hg (II) solution and the analyte was deposited by applying a potential of −0.6 V from 100 up to 350 seconds. The DPV was recorded in acetate buffer with pH=5.0. It was observed an increase of the analytical signal followed by a plateau. We have chosen a deposition time of 300 s as a compromise between a short analysis time and a low LOD (Figure S-4).

The effect of the reduction potential on the analytical signal was studied by varying the reduction potential from -0.4 to −0.8 V. The reduction was carried out for 300 sec using a standard solution with a concentration of 1 μg L^{-1} Hg (II) prepared in 0.1 M acetate buffer pH 5.0. The highest analytical signal was obtained at −0.6 V (Figure S-5).

The dependence of DPV analytical signal on the pH and the composition of the stripping solution was investigated using a standard solution of 1 μg L^{-1} Hg (II), a reduction potential of -0.6 V and a reduction time of 300 s. The pH was optimized in the 2.0 to 7.0 range. The maximum analytical signal was obtained for a pH =5.0 (Figure S-6).

Analytical figures of merit

The analytical performances of the Ag-bipy-CP/PMB/GCE were established for the determination of Hg (II), Cu (II) and Pb (II) ions. The calibration graphs obtained using the developed Ag-bipy-CP/PMB/GCE at optimized conditions indicated the linear dependence of peak current. The linearity ranges are from 0.2 to 10 μg L^{-1} for Hg(II), from 1.3 to 6.4 μg L^{-1} for Cu(II), and from 4.1 to 20.7 μg L^{-1} for Pb(II). The calibration graphs are: $I(\mu A) = 3.547 \times C_{Hg(II)}$ μg L^{-1} + 0.168, $I(\mu A) = 0.268 \times C_{Cu(II)}$ μg L^{-1} - 0.098, $I(\mu A) = 0.056 \times C_{Pb(II)}$ μg L^{-1} + 0.0006 (figure S-7).

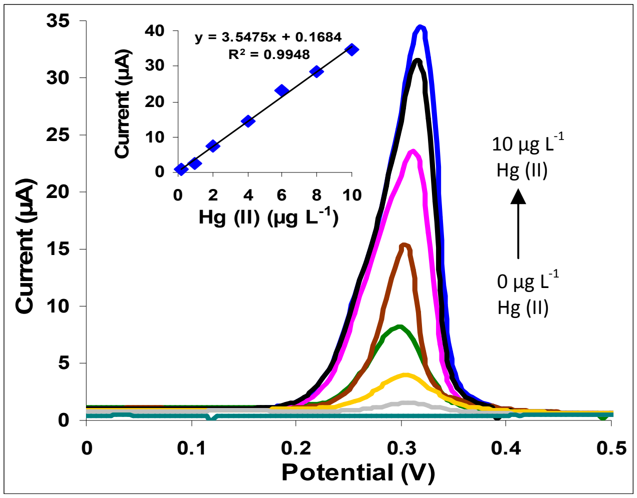


Figure 3. Differential pulse voltammograms recorded for GC-modified electrode and calibration plots obtained for Hg (II) concentrations: 0; 0.2; 1; 2; 4; 6; 8 and 10 μg L^{-1} Stripping conditions: 0.1 M buffer acetate (pH = 5.0);

The detection limits were calculated as the concentration that produces an analytical signal equal with 3.29 σ (standard deviation) of the background noise acquired by 10 voltammetric scans of the analyte-free support electrolyte solution. The obtained limits of detection are: 0.09 μg L^{-1} for Hg(II), 0.71 μg L^{-1} for Cu(II) and 2.3 μg L^{-1} for Pb(II). The best limit of detection was obtained for Hg (II) determination (figure 3). The obtained detection limits are better or similar with the ones reported in the literature for metals detection by stripping using different electrodes modified with nanoparticles, but our Ag-bipy-CP/PMB/GCE has good stability and allows the simultaneous detection of three analytes (table S-2). These studies conclude that Ag-bipy-CP/PMB/GCE modified electrode can be used for the determination of heavy metals and has higher sensitivity for Hg (II).

The figure 4 presents the analytical signals obtained for analyzed ions Hg (II), Cu (II), Pb (II) at different concentrations and shows the influence of Cu (II) and Pb (II) ions on the Hg (II) peak. The DPV peaks are distinct and appear at different values of the potential: Pb (II) at - 0.54 V; Cu (II) at - 0.07 V and Hg (II) at + 0.3 V. The measurement have good reproducibility demonstrated by the RSD values (n=10) that are similar for all three analytes: 3.2% for 4 μg L^{-1} Hg(II), 4.5% for 4 μg L^{-1} Cu(II) and 3.9% for 12.4 μg L^{-1} Pb (II).

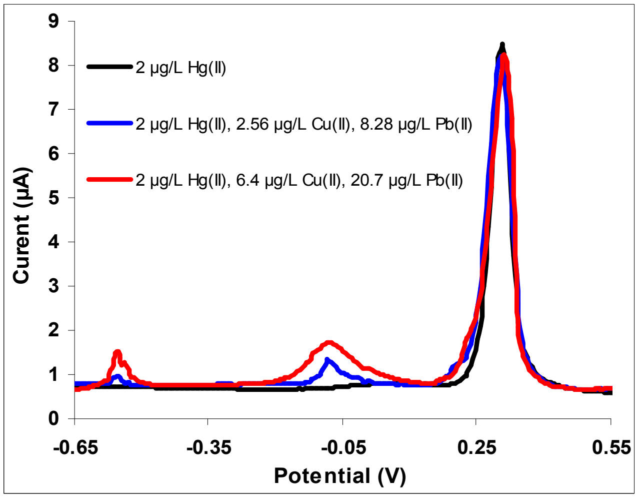


Figure 4. Differential pulse voltammograms recorded for GC-modified electrode obtained for 2 μg L^{-1} Hg(II); 2 μg L^{-1} Hg(II), 2.56 μg L^{-1} Cu(II), 8.28 μg L^{-1} Pb(II) and 2 μg L^{-1} Hg(II), 6.4 μg L^{-1} Cu(II), 20.7 μg L^{-1} Pb(II). Stripping conditions: 0.1 M buffer acetate (pH = 5.0).

Interference study

The potential interferences from several metal ions were tested using standard solutions. Cd (II), Mg (II), As (III) and Cr (II) were tested at possible interferents. It was observed that these metal ions do not produce any analytical signal at 10 μg L^{-1} and do no influence the analytical signals of the analytes (Hg (II), Cu (II), Pb (II)). Even at higher concentration, 50 μg L^{-1} the tested ions does not appear any analytical signal in DPV.

The analytical signals are not changed by the concomitent presence in the sample of Cu (II), Pb (II) and Hg (II). For example, in figure 4 are presented the analytical signals obtained for 2 µg L^{-1} Hg (II) when is detected alone or in mixtures with Cu (II) and Pb (II). These result indicate that all three analytes can be detected together in complex samples with minimum interferences from other heavy metal ions.

Real sample analysis

Fish accumulate methyl mercury from water as they feed on aquatic organisms. Acidic digestion is used to convert organometallic Hg from fish samples into Hg (II) [27, 28]. The developed method was applied to determine mercury in cod and tuna fish samples. Our developed Ag-bipy-CP/PMB/GCE was used for the analysis of Hg (II) from predatory fishes (cod and tuna). The fish samples were digested with concentrated acid solutions prior to the DPV measurements. The fish samples were analyzed directly and spiked with 83.3 and 416.5 µg kg^{-1} Hg (II) (added over fish before digestion).

Table 1. Detection of Hg (II) in fish samples and tests of acids used for digestion using the developed Ag-bipy-CP/PMB/GCE. Values represent the average of three determinations

Sample	Hg(II)	Recovery %
cod	7.5 µg kg^{-1}	-
cod + 83.3 µg Hg(II)	91.6 µg kg^{-1}	101
cod + 416.5 µg Hg(II)	439 µg kg^{-1}	103
tuna	-	-
tuna + 83.3 µg Hg(II)	90 µg kg^{-1}	108
tuna + 416.5 µg Hg(II)	396 µg kg^{-1}	95
Acids used for digestion	-	-
Acids + 1 µg L^{-1} Hg(II)	0.9 µg L^{-1}	90
Acids + 5 µg L^{-1} Hg(II)	4.7 µg L^{-1}	94

Two blank analyses were also carried out by the same protocol: (i) the acids mixture to confirm the absence of reagents contamination with Hg (II) and (ii) 83.3 and 416.5 µg kg^{-1} Hg (II) added over the acids mixtures to investigate the possible analyte loss. Only in cod sample we found 7.5 µg kg^{-1} Hg (II) and the recovery percentages in fish samples are between 95 and 108 %. In acids there was not found any mercury and the recovery of the added Hg (II) was between 90 and 94 % (Table 1).

The plant samples were also digested in acidic solution before subjected to analysis by DPV. The table 2 presents the results obtained from the analysis of real samples (expressed in µg ions per kg dry plant) using the developed Ag-bipy-CP/PMB/GCE. We found mercury ions in *Alchemilla vulgaris* and *Galium verum*. The percentage of recovery was between 90-95 % for the Hg (II), Cu (II) and Pb (II) ions for the analysis of plant samples. Only in *Alchemia vulgaris* were detected 11.4 µg kg^{-1} Cu (II). Pb (II) was not found in any of the analyzed plants.

Conclusions

The coordination polymer obtained from 4,4'-bipyridine and Ag was shown to be an effective material for electrode modification with applications in analytical chemistry for heavy metal detection. The achieved limits of detection were 0.09 µg L^{-1} for Hg (II), 0.71 µg L^{-1} for Cu (II) and 2.3 µg L^{-1} for Pb (II). Importantly, the sensitivity and stability of the developed modified electrodes allowed their used for determination of heavy metals in fish and plants samples with good recovery of spiked analytes. This paper demonstrates the utility of coordination polymers for the development of electrochemical sensors and opens new area of applications for these versatile materials.

Table 2. Analysis of Pb (II), Cu (II) and Hg (II) in plants samples using the developed Ag-bipy-CP/PMB/GCE. Values represent the average of three determinations.

Plant samples	Pb(II) (µg kg^{-1})	Cu(II) (µg kg^{-1})	Hg(II) (µg kg^{-1})	Recovery %
Alchemilla vulgaris	-	11.4	1.67	-
Alchemilla vulgaris+ 15.6µg Cu(II)	-	25.3	1.62	95
Galium verum	-	-	1.6	-
Galium verum+ 5µg Hg(II)	-	-	6	90
Verbascum densiflorum	-	-	-	-
Verbascum densiflorum+ 65µg Pb(II)	60.6			93
Hypericum perforatum	-	-	-	-

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, projects PN-II-RU-TE-2011-3-0076 and PN-II-PT-PCCA-2013-4-0203. The authors are grateful to dr. Andreea Tache for FTIR characterization, dr. Vasile Sorin Manoiu for TEM images.

Notes and references

[a] Centre of Bioanalysis, National Institute of Research and Development for Biological Sciences, 296, Splaiul Independentei, Bucharest 060031, Romania; email: bucurica@yahoo.com

[b] Faculty of Applied Chemistry and Materials Science, Politehnica University of Bucharest, 1-7, Polizu, Bucharest 011061, Romania; email: gl_radu@chim.upb.ro

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

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Graphical abstract

Nanoparticles of 4,4’-bipyridine-silver coordination polymer were used for the modification of glassy carbon electrode with applications in analytical chemistry.