# **Poly(pyrrole-EDTA like) modified electrodes for mercury ions electroanalysis**

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Complexing polymer-coated electrodes synthesized by oxidative electropolymerization of N,N′-ethylenebis[N-[(3-(pyrrole-1 yl)propyl) carbamoyl)methyl]-glycine] (**L**) were used for the electrochemical detection of Hg(II) ions by means of the chemical pre-concentration-anodic stripping technique. Competitive complexations of Hg(II) and Cu(II) or Hg(II) and Pb(II) into C/poly**L** modified electrodes of different film thicknesses were carried out using increasing pre-concentration times. Optimized conditions for mercury ions analysis with poly**L** films were established upon varying experimental parameters such as *p*H, reduction potential, and accumulation and reduction times. Imprinted polymer-coated electrodes prepared by electropolymerization of **L** in the presence of metal cations were used for mercury sensing.

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# **1. Introduction**

Monitoring heavy metal ion levels in drinkable water supplies is essential for human health and safety. There are numerous health problems associated with exposure to high levels of metal ions such as  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $As^{3+/5+}$ because of their tendency to accumulate in the body, their toxicity and their low rate of clearance. For instance, the biological half-life of cadmium is 10–30 years, while that of lead in bones is more than 20 years [1]. The Environmental Protection Agency (US EPA) estimates that nearly 20 % of human exposure to lead occurs through contaminated drinking water [2]. It is therefore critical for humans to experience minimal exposure to these contaminants and to develop reliable tools allowing fast and accurate quality monitoring.

Anodic stripping voltammetry as well as adsorptive stripping voltammetry are very sensitive electrochemical techniques suited for the determination of trace metals [3- 7]. This strategy is based on reductive step using mercury or solid electrodes, followed by anodic stripping of the electrodeposited metal. The analytical scope of solid electrodes can be moreover greatly extended through appropriate surface engineering [8-11] such as coating with complexing polymer materials. Modification of working electrodes with ion selective molecular hosts is especially pursued in order to enhance the selectivity and sensitivity of electroanalytical measurements, or/and to prevent electrode fouling. The other important advantage of modified electrodes is to enable accumulation and measurement steps at the same electrode surface. No further time-consuming procedure is required to elute target analytes into suitable medium required for

measurement. In many cases, electrode surface may be easily electrochemically regenerated in-situ at the end of the analysis procedure and highly reproducible analytical results may be obtained. Conducting polymer films have therefore received considerable attention for their numerous potential applications in analysis and particularly for the detection of trace metals in contaminated samples [11, 12].

Polypyrrole is one of the most extensively used conducting polymers considered to elaborate various types of analytical sensors [13-15]. Incorporation of complexing fragments into such polymeric material can be accomplished efficiently by direct electropolymerization of pyrrole appended complexing monomers [16, 17]. Stable functionalized polymers with controlled size and sites concentration could be produced following this strategy and they can be used for the determination of trace metals [18]. During the accumulation step performed at open circuit, the thermodynamic and kinetic features of the heterogeneous metal-ligand complexation process determine the sensitivity and selectivity of the targeted analytical measurements.

The complexing properties of poly(N,N' ethylenebis[N-[(3-pyrrole-1-l)propyl)carbamoyl)methyl] glycine) coated electrodes were previously examined towards  $Cu(II)$ ,  $Pb(II)$  and  $Cd(II)$  cations. We clearly established that the selectivity of molecular electrode materials can be subtly modulated upon playing on the accumulation time and on the morphology of the complexing polymers [19].

In the present article, we report a thorough investigation on mercury(II) sensing properties of poly(N,N'-ethylenebis[N-[(3-pyrrole-1-yl)propyl)

carbamoyl) methyl]-glycine) coated glassy carbon electrodes (C/poly**L**) using the chemical preconcentration- anodic stripping technique. We particularly clearly reveal that C/poly**L** electrodes are selective for mercury ions in the presence of other ions like Cu(II) and  $Pb(II)$ .

#### **2. Experimental**

#### **2.1 Reagents and materials**

The synthesis of (N,N'-ethylenebis[N-[(3-pyrrole-1 yl) propyl)carbamoyl) methyl]-glycine) was performed according to a previously reported procedure [19]. Acetonitrile (Rathburn, HPLC grade S) was used as received. Tetra-n-butylammonium perchlorate (TBAP, Fluka puriss) was dried under vacuum at 80  $^{\circ}$ C for 3 days. Suprapur grade sodium acetate and acetic acid (Merck) were used to prepare  $0.1 \text{mol L}^{-1}$  acetate buffers. Copper(II) acetate -Cu(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>,H<sub>2</sub>O, lead(II) nitrate - Pb(NO<sub>2</sub>)<sub>2</sub>, mercury(II) acetate -  $Hg(CH_3CO_2)_2$  and anhydrous zinc(II) trifluoromethanesulfonate –  $(CF_3SO_3)_2\text{Zn}$  were used as source of metal ions. Copper(II) acetate and lead(II) nitrate were from Prolabo. Mercury(II) acetate and Zn-trifluoromethanesulfonate were purchased from Strem. All reagents were used without further purification. Perchloric acid was obtained from Merck. Disodium salt of ethylenediamine tetraacetic acid (EDTA) and sodium dithionite were purchased from Loba Chemie. Distilled water was obtained from an Elgastat water purification system ( $5M\Omega$  cm).

#### **2.2 Electrochemical equipment**

Electrochemical experiments were performed with a PG STAT 12 Autolab potentiostat, using a conventional three-electrode system. The working electrode was a carbon disk (3mm diameter, from CH Instruments). The counter electrode was a platinum wire. The reference electrode used for electropolymerizations was Ag/10mM AgNO<sub>3</sub>,  $0.1M$  TBAP,  $CH<sub>3</sub>CN$ , while that used for electroanalytical experiments was a conventional Ag/AgCl electrode. A Denver-Instrument Model 220 *p*Hconductivity meter was used to measure the *p*H.

#### **2.3 Preparation of the modified electrodes**

Prior to electropolymerization the glassy carbon disk working electrode was polished with 0.2 µm diamond paste. Electropolymerization was performed by controlled potential electrolysis (CPE) at a potential of +0.9V/(Ag/Ag+ ) until reaching the desired charge. Poly**L** films were grown on glassy carbon disk electrodes in acetonitrile solution of  $\bf{L}$  (10<sup>-3</sup>M) in 0.1mol  $\bf{L}$ <sup>-1</sup> TBAP, either containing two-molar equivalents of  $HClO<sub>4</sub>$  using the previously described procedure [19], or containing four-molar equivalents of Zn-trifluoromethanesulfonate. After transfer into pure electrolyte  $CH_3CN + 0.1$ mol  $L^{-1}$ TBAP, the modified electrodes exhibit the regular

electroactivity of N-substituted polypyrroles [20]. Films with apparent surface coverages in complexing sites  $(\Gamma_L)$ between  $8 \times 10^{-10}$  and  $2 \times 10^{-9}$  mol cm<sup>-2</sup> were typically obtained using polymerization charges of 0.3 to 1mC.  $\Gamma_{\text{L}}$ was determined from the charge recorded under the polypyrrole oxidation wave measured by cyclic voltammetry (CV) at the scan rate of 2mV/s, taking into account that one ethylenediaminotetracetamide group is attached to 2 pyrrole rings and assuming that one in three pyrrole units is oxidized [21].

Modified polypyrrole films usually exhibit high background currents leading to major limitation of the electrochemical window and thereby making metal detection difficult [22]. We used a straightforward solution to this problem by overoxidizing polypyrrole [23-25]. Before each analytical experiment, the pyrrole-based electroactivity was therefore destroyed upon cycling the electrode potential (5 cycles) between -0.2 V and +1.2V in a buffer acetate ( $pH = 4.5$ ). This treatment lead to C/poly**L** electrodes covered with non-conducting polymer that have been used for all our electrochemical investigation.

#### **2.4 Accumulation and voltammetric procedures**

Accumulation of metal ions into poly**L** films was carried out at open circuit upon dipping the C|poly**L** modified electrodes for a given time into 5mL stirred buffer solution (usually at a  $pH = 4.5$ ) containing a given metal salt. The electrodes were then removed from the accumulation cell and thoroughly washed with purified water to remove uncomplexed ions from the modified electrode surface. After transferring the latter into an electroanalytical cell containing 0.1M acetate buffer solution, the accumulated metal ions were reduced at a specific potential during a specifically established reduction time (see Section 3.4). Then a differential pulse voltammetry (DPV) experiment (10mV s<sup>-1</sup>) was performed under quiescent conditions. Each analysis aiming to sense the entrapped metallic species was accomplished with a freshly modified electrode.

## **3. Results and discussion**

#### **3.1 Complexation of mercury in homogenous phase**

The mercury ion binding properties were first investigated by cyclic voltammetry in acetate buffer (*p*H 4.5,  $v = 0.25Vs^{-1}$ , glassy carbon electrode; Ag/AgCl reference electrode). The cyclic voltamogramm recorded for an aqueous solution of free mercury shows a redox couple having a peak at -0.14V and a shoulder in the cathodic scan and two anodic peaks at +0.44 and 0.63 V/(Ag/AgCl). In the presence of one molar equivalent of **L**, no clear reduction peak could be observed in the range of accessible potentials. The anodic stripping peaks are not so much affected by the addition of **L** (Fig. 1). This behaviour is similar with what it was observed with copper and lead [19].

## **3.2 Complexation of mercury with PolyL**

The complexing properties of poly**L** materials, synthesized by electropolymerization of **L** in CH<sub>3</sub>CN + 0.1M TBAP in the presence of two-molar equivalents of HClO<sub>4</sub>, were investigated using the chemical pre-<br>concentration-anodic stripping method described concentration-anodic stripping method previously [18, 19]. Dipping a freshly prepared modified electrode into an aqueous 0.1M acetate buffer solution containing mercury ions led to the complexation within the polymer film (chemical accumulation at open circuit). After this accumulation step, the modified electrode was transferred into a metal-free aqueous 0.1M acetate buffer solution, in which the collected metal ions were reduced before recording the stripping currents using DPV. Typical DPV curve obtained after 10 minutes of accumulation in 10-5 M mercury(II) exhibits a stripping peak around 0.4V/(Ag/AgCl) corresponding to the oxidation of mercury(0) to mercury(II) ion. Trying to regenerate the modified electrode by dipping the C/poly**L**-mercury electrode into EDTA or dithiocarbamate solutions as decomplexing agents we noticed that the Hg(II) was not entirely removed. The failure to completely remove  $Hg^{2+}$ after each experiment could be explained by a strong affinity of poly**L** toward mercury ion due to the EDTA structures and to the additional carbonyl groups in the polymer backbone generated by overoxydation of pyrrole [26].



*Fig. 1. Cyclic voltammograms (25 mV/s) recorded on glassy carbon electrodes in 5*´*10-4 M Hg(OAc)2 - bolded*   $\lim_{\epsilon \to 0}$  *and in*  $5\times10^{4}$ *M* equimolar mixture of  $Hg(OAc)_{2}$  *and L - doted line; 0.1M buffer acetate (pH 4.5).*

Due to the fact that we have not been able to remove the entire amount of Hg(II) ions from the poly**L** film, each measurement was consequently performed with freshly prepared modified electrodes. The reproducibility of Hg(II) analyses was examined with freshly C/poly**L** electrodes modified by electropolymerization in  $10^{-3}$ M solution of monomer **L**: ten electrodes with charges of 0.5mM and ten electrodes with charges of 1mC. Each modified electrode was dipped for  $10$ min into a  $10^{-5}$ M Hg(II) solution. The corresponding stripping currents showed relative standard deviations of 4.9 % and 2.37 %, respectively which shows a good reproducibility of the elaboration process.

# **3.3 Competitive complexation of Hg, Cu and Pb ions**

Dipping the modified electrodes into aqueous 0.1M acetate buffer solution containing mercury, copper and lead ions led to their complexation within the polymer film. After the accumulation step in open circuit, each modified electrode was transferred into a metal-free aqueous 0.1M acetate buffer solution, in which the collected metal ions were reduced before recording the stripping currents using DPV. The DPV curves obtained in an equimolar mixture of  $Hg(II)$ , Cu(II) and Pb(II) ions after 10-min of accumulation time (Figure 2) revealed the higher affinity of poly**L** for Hg(II) ions.



*Fig. 2. DPV curves recorded at C|polyL electrodes of different polymerization charges in 0.1M aqueous acetate buffer (pH = 4.5) after 10min of pre-concentration in 10–*  ${}^5M$  Hg(II), Cu(II) and Pb(II) acetate buffer solution. *Depositionof metals was performed at – 1.8V for 3min.*

Competitive complexations of Hg(II) and Cu(II) or Hg(II) and Pb(II) into C/poly**L** modified electrodes were carried out at *p*H 4.5, using increasing accumulation times (from 1 to 25 min) and different film thicknesses  $(8\times10^{-10}$ moles/cm<sup>2</sup> to  $2\times10^{-9}$  moles/cm<sup>2</sup>). Figs. 3 and 4 show the intensity of the stripping peak currents corresponding to the dissolution of Hg and Cu or Hg and Pb, as a function of the accumulation time in equimolar  $10^{-5}M$  solutions containing either Hg(II) and Cu(II), or Hg(II) and Pb(II).

The results from figures 3 and 4 indicate that the extraction selectivity depends on both film thickness and accumulation time. In the case of mercury ions the peak intensity increases with the accumulation time and reaches a maximum at around 8 min, then it shows a slight decrease until reaching a plateau after 10 min. The film thickness clearly influences the height of the stripping peak for mercury ions. When increasing the film thickness, the intensity of the redissolution peak increases due to the increased concentration in complexing sites. The intensity of the copper-based stripping peak also increases with the accumulation time to reach a maximum value then decreases and reaches another stable value. Conversely, the intensity of the lead stripping peak decreases with increasing accumulation time. For thick films and short

accumulation times we surprisingly observed larger stripping peaks with lead than with mercury ions.



*Fig. 3. Stripping peak currents obtained with C/polyL electrodes as a function of the accumulation time in an equimolar aqueous solution (10<sup>5</sup>M) of Cu(II) and Hg(II); acetate buffer, pH 4.5; films of different thicknesses were obtained by EPC using charges of 0.3 (A), 0.5 (B) and 1 (C) mC in a solution of L (1mM) in 0.1M TBAP, CH3CN.*

The accumulation time and film thickness influences were also studied for mixtures of Hg(II), Cu(II) and Pb(II)  $(10^{-5}M)$ . The curves shown on Figure 5C reveal that copper and lead cations could compete with mercury ions when using thick films at short accumulation times (less than 5min), while after this time the film shows a greater afinity for mercury ions.

All these observations clearly demonstrate that the determination of mercury(II) ions with poly**L** modified electrodes is strongly favored as compared to that of lead(II) and copper(II) ions. These results are in agreement with the complexation thermodynamic constants ( $log_{10} Kf$ , 20°C, 0.1M) of the metal ions with EDTA: 21.70 for Hg(II); 18.80 for Cu(II); and 18.04 for Pb(II) [27] which confirms the higher affinity of this EDTA-like ligand towards mercury.



*Fig. 4. Stripping peak currents obtained with C/polyL electrodes as a function of the accumulation time in an*  equimolar aqueous solutions (10<sup>5</sup>M) of Pb(II) and *Hg(II); acetate buffer, pH 4.5; films of different thicknesses were obtained by EPC using charges of 0.3 (A), 0.5 (B) and 1 (C) mC in a solution of L (1mM) in 0.1M TBAP, CH3CN.*

## **3.4 Optimized conditions for mercury ions analysis**

Several parameters, related to the accumulation (*p*H, accumulation time) and electrochemical reduction (reduction potential and time) steps were varied to improve the cation sensing capability of C/poly**L** towards Hg(II) ions. Fig. 6 shows the *p*H dependency of the mercury-based stripping current in 0.1M sodium acetate/acetic acid buffer solutions. This study was achived with poly**L** modified electrodes obtained by EPC using a polymerization charge of 0.5mC which were dipped in a 10-5 M mercury solution for 10min accumulation time and then kept at -1.8V/(Ag/AgCl) for 2 minutes and DPV scanned. The current responses are slightly affected by the *p*H of the accumulation solution (in the investigated range), reaching an optimum value around *p*H 4.5. Therefore, the *p*H of the accumulation solution was selected at this value in the following experiments.



*Fig. 5. Stripping peak currents obtained with C/polyL electrodes as a function of the accumulation time in an equimolar aqueous solutions (10-5 M) of Cu(II), Pb(II)*  and Hg(II); acetate buffer, pH 4.5; films of different *thicknesses were obtained by EPC using charges of 0.3 (A), 0.5 (B) and 1 (C) mC in a solution of L (1mM) in 0.1M TBAP, CH3CN.*



*Fig. 6. Variation of the mercury redissolution peak with the pH of accumulation solution; 10min accumulation time in acetate buffer solutions of*  $10^{-5}M$  *Hg (II); the reduction was performed at -1.8V/(Ag/AgCl) for 2min.*

The effect of the accumulation time (in open circuit) was studied with films of different thicknesses obtained at three polymerization charges (Fig. 7). The poly**L** electrode was immersed in an acetate buffer containing mercury ions  $(10<sup>-6</sup>M)$  at *p*H 4.5. The peak currents increase and reach a plateau at 10min. Therefore, the accumulation time was set to 10 minutes for all our experiments.



*Fig. 7. Influence of the accumulation time on the mercury redissolution peak for C/polyL modified electrodes with films of different polymerization charges; Hg(II) in the accumulation solution (acetate buffer, pH 4.5) was 10- 6 M; the reduction was performed* 

 *at -1.8V/(Ag/AgCl) for 2min.* 

Fig. 7 shows an intriguing aspect: as the thickness of the film increases as the recorded currents in DPV decrease. This behavior was observed only in the case of  $Hg(II)$  ions analysis, and not for Cu(II) and Pb(II) [19]. In order to see the effect of the polymer film thickness on the stripping current we checked the influence of the scan rate on the CV anodic peak of polypyrrole oxidation for different film thicknesses (corresponding to different polymerization charges). Figure 8 shows the linear dependences of the currents on the scan rate, which are relevant for a homogeneous diffusion within the film. However, the behavior seen in Fig. 7 is not in agreement with this homogeneous diffusion and it shows higher site activity for thinner layers. This aspect could be explained by the fact that in a thicker film the mercury ions enter only in the upper layer blocking the complexing cavities and preventing the entrance of new ions deep in the polymer (it means smaller amount of mercury ions than the number of complexing sites) and also not all the complexed mercury ions are reduced on the electrode surface.



*Fig. 8. Dependence of the CV anodic peak currents of the C/polyL modified electrodes on the scan rate (in acetonitrile + 0.1M TBAP) obtained at three polymerization charges.*

The dependence of the anodic stripping peak on the reduction potential was examined over the potential range between -1.4 and -2V. We found that a reduction potential of  $-1.8V$  is enough to reduce  $Hg(II)$  in our conditions. Therefore, this potential was kept as the reduction potential in our measurements.

The effect of the reduction time on Hg(II) ions analysis was tested as follows: the modified glassy carbon electrode was immersed for ten minutes in the accumulation solution (acetate buffer, *p*H = 4.5, containing mercury ions,  $10^{-5}M$ ), then removed and transferred into blank acetate buffer solution, *p*H = 4.5, where it was reduced at -1.8 V/(Ag/AgCl) for different periods of time. The effect of deposition time is shown in Figure 9. It can be seen that the redissolution peak currents increase as the deposition time increases from 1 to 3 min, and then they reach a plateau. Therefore, the deposition time of 3 min was chosen for further experiments.



*Fig. 9. Variation of the DPV mercury anodic peak with respect to the deposition time; 10min accumulation time*  in acetate buffer solutions of  $10^{-5}M$  Hg(II) at  $pH = 4.5$ ,  *then reduction at -1,8V/(Ag/AgCl).*

#### **3.5 Calibration plots**

Using the best experimental conditions previously found (pH, preconcentration time, reduction potential and reduction time), the C|poly**L** modified electrodes have been used to determine concentrations of Hg(II) ions in aqueous media, using the chemical preconcentrationanodic stripping method (Fig. 10). DPV signals were recorded for various concentrations of metal ions using a freshly prepared electrode for each measurement. Each datum point is the average of 3 measurements.

Linear calibration plots have been obtained for different film thicknesses (Fig. 10B). For the thinnest explored film ( $\Gamma = 8 \times 10^{-10}$  moles/cm<sup>2</sup>) a linear range from  $10^{-8}$ M to  $5\times10^{-7}$ M has been obtained. As expected, the increase of the film thickness results in higher stripping currents. The linear domain obtained for  $\Gamma = 10^{-9}$  mole/cm<sup>2</sup> has values between  $10^{-7}$  and  $2\times10^{-6}$ M, while for a thicker film with  $\Gamma = 2 \times 10^{-9}$  mole/cm<sup>2</sup>, it has been larger between  $10^{-7}$  and  $6\times10^{-6}$ M. As it can be seen on Fig. 10A, the stripping peaks obtained for the lowest concentration of mercury ions are higher with thin films; they show a rapid increase with concentration and reach a limit after about  $5 \times 10^{-7}$ M. For thicker films the plateau is reached at higher concentrations  $(3\times10^{-6}M \text{ for } \Gamma = 10^{-9} \text{mole/cm}^2$  and  $6\times10^{-7}$ <sup>6</sup>M for  $\Gamma = 2 \times 10^{-9}$  mole/cm<sup>2</sup>) due to the increase in the amount of complexing sites in the polymer film. This observation was lined out also in Fig. 11 in which it was shown the influence of the film thickness for two different concentrations of mercury ions  $(10^{-5}$  and  $10^{-6}$ M). It can be observed an increase of the stripping currents with polymerization charge (which is proportional with the film thickness), followed by a slight decrease after an optimum. For the lowest concentration  $(10^{-6}M)$  the optimum of the stripping peak is obtained for thinner films (lower polymerization charges of about 0.3mC), while for the concentration of  $10^{-5}M$  the optimum film thickness corresponds to 0.7mC. This shows that the film thickness should be adapted to the range of concentrations, which are determined in order to get an optimum response.



*Fig. 10. A) DPV peak currents recorded at (□) 0.3mC (Γ*   $\approx$  8×10<sup>-10</sup> moles/cm<sup>2</sup>), (▲) 0.5mC ( $\Gamma \approx$ 10<sup>-9</sup> moles/cm<sup>2</sup>) and ( $\circ$ ) 1mC ( $\Gamma$  ≈2×10<sup>-9</sup>moles/cm<sup>2</sup>) C/polyL electrodes as a *function of Hg (II) concentrations (acetate buffer, pH = 4.5, accumulation for 10min under stirring, 3min reduction time at -1.8V(Ag/AgCl). B) Linear parts of the calibration plots.* 



*Fig. 11. Variation of the anodic stripping peak intensity obtained for C/polyL modified electrodes with the polymerization charge for two different mercury ion concentrations* (10<sup> $6$ </sup> and 10<sup> $5$ </sup>M) in buffer acetate, pH  *4.5.*

# **3.6 Imprinted C/PolyL electrodes for Hg(II) analysis**

In order to improve the mercury sensing the electropolymerization of **L** was performed using imprinted electrodes. They were obtained by the same electropolymerization procedure in 1mM solution of **L** in  $0.1M$  TBAP/acetonitrile, but in the presence of  $Hg(II)$  ions (4 equivalents). The modified electrode was then immersed in EDTA or sodium dithiocarbamate solutions  $(10<sup>-2</sup>M)$  for 10 min under stirring in order to get the metalfree modified electrode. Unfortunately, we could not obtain the mercury free electrodes. This was probably due to the fact that the complexation constant is very high and Hg(II) ions can not be expelled from the film. We consequently tried to obtain imprinted electrodes using  $Zn(II)$  or Cd  $(II)$  ions instead of  $Hg(II)$  ions. The best results were obtained when the electropolymerization of **L** was performed in the presence of 4-molar equivalents of zinc cations. Under these experimental conditions, electropolymerization occurs well because all basic amine groups in **L** are complexed with Zn(II) metal ions. In this case, the decomplexation was performed by immersion the imprinted electrode in 0.01M EDTA solution and checked by DPV in the potential range of anodic stripping. In these conditions the reduction of Zn(II) ions and the stripping are not seen as they occur near the hydrogen wave [28].

These imprinted electrodes were compared with the non-imprinted ones in respect to Hg(II) analysis. Figure 12 shows that even if the intensity of the stripping peak is smaller with imprinted polymers, the linear domain with mercury ion concentration is larger  $(10^{-8} - 10^{-6}M)$  and the detection limit decreases to  $10^{-8}$  M.



*Fig. 12. DPV peak currents recorded using (•) C|polyL electrodes (0.5mC,*  $\Gamma_L \approx 10^{-9}$  *mol cm<sup>-2</sup>)* and  $(\triangle)$  *imprinted C*|polyL electrodes (0.5mC ( $\Gamma$ <sub>L</sub>  $\approx$  9×10<sup>-10</sup>mol cm<sup>-2</sup>) as a *function of Hg (II) concentration in the accumulation solution (acetate buffer, pH = 5.5); 12min preconcentration; reduction of metal ions at -1.8V(Ag/AgCl) for 3min; each point is the average between 3 measurements. Inset: linear parts of the calibration plots.*

## **4. Conclusions**

Modified electrodes with the poly(N,N' ethylenebis[N-[(3-(pyrrole-1-yl) propyl) carbamoyl) methyl]-glycine) were tested with respect to the complexation properties towards Hg(II) ions. Competitive complexation of  $Hg(II)$  and  $Cu(II)$ , or  $Hg(II)$  and  $Pb(II)$ , in these modified electrodes showed greater affinity towards  $Hg(II)$  ion than  $Cu(II)$  and  $Pb(II)$  ions. These modified electrodes were used to determine the mercury ion leading to linear ranges of concentration between  $10^{-7}$  -  $2\times10^{-6}$ M, and  $10^{-8}$  -  $10^{-6}$ M for non pre-structured polymers and imprinted polymers, respectively.

The results demonstrated the great potential of these chemically modified electrodes in analytical chemistry to achieve selective mercury sensing.

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# **References**

- [1] R. A. Goyer, in: C. D. Klaassen (Ed.), Toxicology, The Basic Science of Poisons, fifth ed., McGraw- Hill, New York, 691, 1996.
- [2] Lead in Drinking Water, http://www.epa.gov/safewater/lead/leadfacts.
- [3] J. Wang, Stripping Analysis: Principles, Instrumentation and Applications, VCH, Weinheim, 1985.
- [4] G. Henze, R. Neeb, Elektrochemische Analytik, Springer, Heidelberg, 1986.
- [5] G. Henze, in Ullmann's Encyclopedia of Industrial Chemistry, Vol. B5, VCH, Weinheim, 1994.
- [6] J. Wang, Analyst **199**, 763 (1994).
- [7] S. Sander, G. Henze, Fresenius J. Anal. Chem. **349**, 654 (1994).
- [8] D. W. M. Arrigan, Analyst **119**, 1953 (1994).
- [9] J. Wang, N. Foster, S. Armalis, D. Larson, A. Zirino, K. Olsen, Anal. Chim. Acta **310**, 223 (1995).
- [10] J. Wang, J. Lu, B. Hcevar, P. A. M. Farias, B. Ogorevc, Anal.Chem. **72**, 3218 (2000).
- [11] M. D. Imisides, R. Jhon, P. J. Riley, G. G. Wallace, Electroanalysis **3**, 879 (1991).
- [12] K.-K. Shiu, O.-Y. Chan, S.-K. Pang, Anal. Chem. **67**, 2828 (1995).
- [13] A. Ramanavicius, A. Ramanaviciene, A. Malinauskas, Electrochim. Acta **51**, 6025 (2006).
- [14] T. A. Bendikov, J. Kim, T. C. Harmon, Sens. Actuators B **106**, 512 (2005).
- [15] S. B. Adeloju, G. G. Wallance, Analyst **121**, 699 (1996).
- [16] Q. Cai, S. B. Khoo, Anal. Chem. **66**, 4543 (1994).
- [17] U. Lange, N. V. Roznyatovskaya, V. M. Mirsky, Analytica Chimica Acta **614**(1), 1 (2008).
- [18] M. Heitzmann, L. Basaez, F. Brovelli, C. Bucher, D. Limosin, E.Pereira, B. L. Rivas, G. Royal, E. Saint- Aman, J.-C. Moutet, Electroanalysis **17**(21), 1970 (2005).
- [19] M. Heitzmann, C. Bucher, J-C. Moutet, E. Pereira,

 B-L. Rivas, G. Royal, E. Saint-Aman, Electrochim. Acta **52**, 3082 (2007).

- [20] J.-C. Moutet, A. Zouaoui, Electrochim. Acta **46**, 4035 (2001).
- [21] G. K. Chandler, D. Pletcher, Electrochemistry, Specialist Periodical Reports, Royal Society of Chemistry, London, 117, 1986.
- [22] A. Wanekaya, O. A. Sadik, J. Electroanal. Chem. **537**, 135 (2002).
- [23] D. W. M. Arrigan, D. S. Gray, Anal. Chim. Acta **157**, 402 (1999).
- [24] H. Shiigi, H. Yakabe, M. Kishimoto, D. Kijima, Y. Zhang, U. Sree, B. A. Deore, T. Nagaoka, Microchim. Acta **143**, 155 (2003).
- [25] H. Shiigi, D. Kijima, Y. Ikenaga, K. Hori, S. Fukazawa, T. Nagaoka, J. Electrochem. Soc. **152**, 129 (2005).
- [26] E. Reza Ansari, J. of Chemistry **13**, 186 (2006).
- [27] A. E. Martel, R. M. Smith, Critical Stability Constants **1 – 3**, Plenum Press, New York, 1977.
- [28] M. G. Constant van den Berg, J. Z. Sirichai Dharmvani, Limnol. Oceanogr. **29**(5), 1025 (1984).

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