New azulene modified electrodes for heavy metal ions recognition

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(E)-2-thioxo-5-((4,6,8-trimethylazulen-1-yl)methylene)thiazolidin-4-one (**L**) was electrochemically characterized by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode voltammetry. Poly**L** modified electrode obtained by the controlled potential electrolysis was tested in solutions containing different metal ions (Cd, Pb, Cu, Hg) at increased concentrations. The best response was found for Pb (10^{-7} M).

Key words: (E)-2-thioxo-5-((4,6,8-trimethylazulen-1-yl)methylene)thiazolidin-4-one, cyclic voltammetry, differential pulse voltammetry, rotating disk electrode voltammetry, heavy metal ions detection

INTRODUCTION

Benzylidene rhodanines, especially those containing electron rich groups as dimethylamino groups, have been used for amperometric [1] and spectrofotometric determination of metal ions such as Cu (II), Fe (II), Ni (II) and Zn (II) [2]. They give good results in preconcentration of silver by quantitative complexation during the samples analysis by flame atomic absorption spectrometry (FAAS) [3]. Due to high affinity to silver, benzylidene rhodanines can be used for indirect titration of anions that form precipitates with silver nitrate, such as cyanide [4]. Other metals that can be dosed quantitatively using these compounds are Hg, Cu, Au, Pt and Pd, according to the Merck index. Here, azulenylvinyl rhodanines that are similar to benzylidene rhodanines, were synthesized and tested as good complexants for toxic cations like Cu (II), Pb (II) and Hg (II).Azulenes are polar organic compounds characterized by two condensed cyclic moieties; one cycle moiety containing seven carbon atoms (electron-poor) and the other one containing five carbon atoms (electron-rich) [5]. These properties have been exploited for–preparation of polymer films which have been used for heavy metal ions detection [6], applications in optoelectronics [7] and medicine (antiretroviral activity) [8]. This article presents the electrochemical characterization of the azulene derivative (E)-2-thioxo-5-((4,6,8-trimethylazulen-1-yl)methylene)thiazoclidin-4-one

(**L**) (Fig. 1). A new modified electrode based on the poly**L** has been prepared and used for detection of heavy metals Cu (II), Pb (II), Hg (II) and Cd (II) in different concentrations
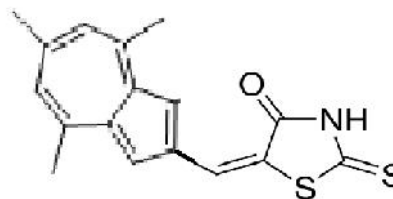

Fig. 1. Structure of azulene derivative **L**.

EXPERIMENTAL

The ligand **L** was synthesized according to the previously published procedure [9]. Electrochemical characterization of the ligand **L** and preparation of modified electrodes were performed in acetonitrile (CH_3CN) containing 0.1M tetrabutylammonium perchlorate (TBAP), both from Fluka, and used as solvent and supporting electrolyte. Stock solutions of Cd, Pb, Cu and Hg (10^{-2}M) have been freshly prepared before each experiment, using Cd (II) nitrate tetra hydrate, Pb(II) nitrate and Hg(II) acetate (all Sigma Aldrich) and Cu(II) acetate monohydrate (Fluka). 0.1 M buffer acetate (pH = 5.5) solution was prepared from 0.2 M acetic acid solution and 0.2 M sodium acetate solution.

Electrochemical experiments have been performed using the PGSTAT 12 AUTOLAB

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connected to a three-electrode cell. As working electrodes, a glassy carbon disk (with 3 mm diameter) (Metrohm) and poly**L** glassy carbon modified electrodes were explored in characterization and recognition experiments, respectively.

The auxiliary electrode was a platinum wire, while the reference electrode was either Ag/10 mM AgNO$_3$ in 0.1 M TBAP/CH$_3$CN (in electrochemical experiments performed in acetonitrile solutions), or Ag/AgCl, 3 M KCl (in electrochemical experiments performed in water solutions). The glassy carbon electrode was polished with diamond (2µm) paste before each experiment and cleaned with the solvent.

Cyclic voltammetry (CV), rotating disk electrode voltammetry (RDE) and differential pulse voltammetry (DPV) methods have been used for electrochemical characterization. CV curves have usually been recorded at the scan rate of 0.1 V/s. DPV curves have been recorded at 0.01 V/s, with a pulse height of 0.025 V and step time of 0.2 s, while RDE curves were recorded at 0.01 V/s. All curves have been recorded at 25ºC, under argon atmosphere. In experiments performed in acetonitrile solutions, the potentials were finally referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc$^+$) equal to +0.07 V.

Electrochemical experiments of heavy metal ions detection have been performed in 0.1 M buffer acetate (pH = 5.5) solution as the supporting electrolyte, at 25ºC under argon atmosphere. Heavy metal ion solutions of different concentration (10^{-4} M – 10^{-7} M) were prepared by successive dilution from their stock solutions (10^{-2} M) in water.

RESULTS AND DISCUSSION

Electrochemical characterization of the azulene derivative **L** has been done by CV, DPV and RDE experiments on the glassy carbon electrode. The CV and DPV oxidation and reduction curves have been recorded at different concentrations of **L** (0 – 1mM) in 0.1 M TBAP/CH$_3$CN, starting from the stationary potential (Fig. 2). DPV curves in Fig. 2A show three oxidation peaks (a1 – a3) and two reduction peaks (c1 and c2). DPV peak currents for a1, c1, and c2 peaks are increasing with the concentration of **L**. For a2 and a3 peaks, however, there is an inversion, which will be explained further on. CV curves in Fig. 2B show 4 anodic peaks (a1 – a4) and one cathodic peak (c2), respecting the notation from DPV curves.

Fig. 3A presents the CV curves obtained at different scan rates (0.1 – 1 V/s) within potential domains of the anodic peak a1 and cathodic peaks

c1 and c2 for 0.5 mM solution of **L**. A new cathodic peak (d) can be clearly seen with increase of the scan rate. Also, all current values increase with the scan rate. Linear dependences for the peak currents on the square root of the scan rate are obtained for a1 and c1 (Fig. 3B).
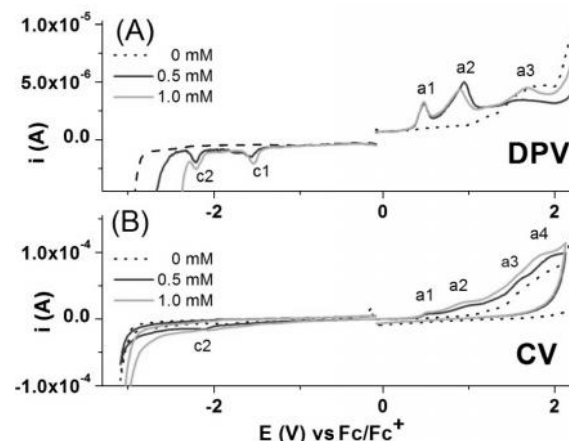

Fig. 2. DPV (0.01 V/s) curves (A) and CV (0.1 V/s) curves (B) of glassy carbon electrode for different concentrations of L in 0.1M TBAP/CH$_3$CN.
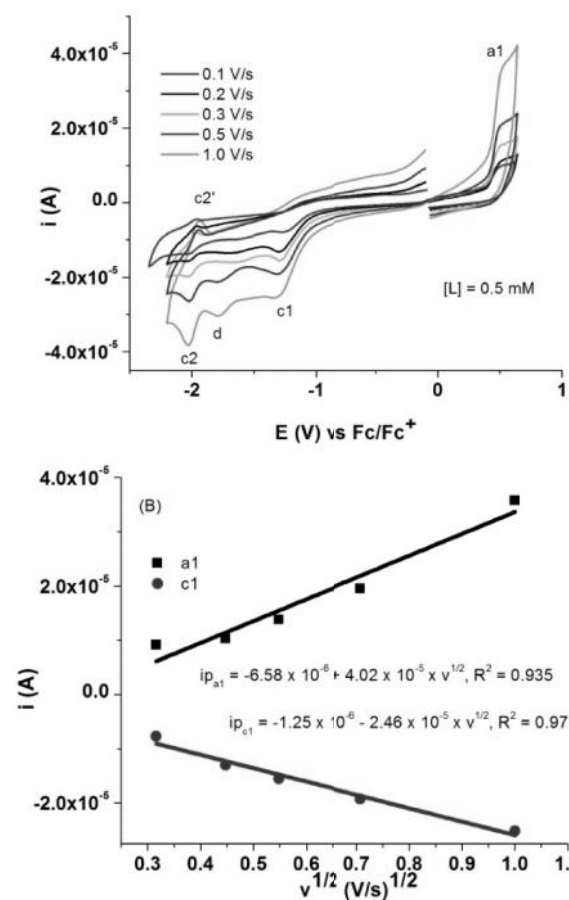

Fig. 3. CV curves in the short potential domain at different scan rates of glassy carbon electrode for 0.5 mM of **L** in 0.1M TBAP/CH3CN (A) and linear dependences of peak currents on the square root of scan rate (B).

The diffusion coefficient of **L** was calculated from the slope of the a1 peak current using the Randles-Sevcik equation for one electron transfer, giving the value of 1.77×10^{-5} cm^2/s.

Fig. 4 shows the CV curves (0.1 V/s) obtained in different scan potential domains for 0.5 mM solution of **L,** while Table 1 presents the character of processes and potential of each peak, all estimated from CV and DPV curves measured for 0.5 mM solution of **L**. It seems that all processes in the anodic domain are irreversible, while in the cathodic domain, the peak c1 is irreversible, while c2 is reversible, having a corresponding peak in the reverse scan (c2') situated at 89 mV in respect to c2.
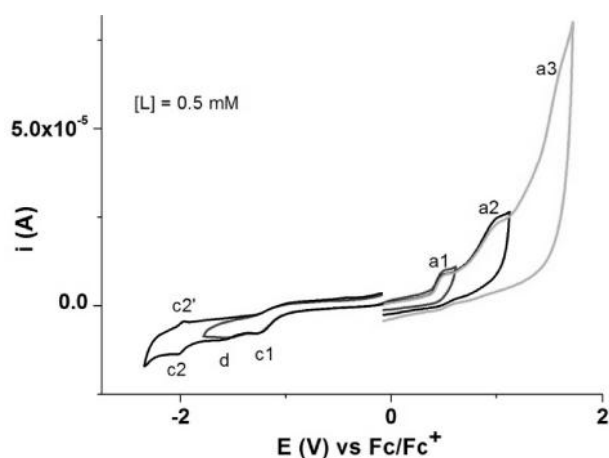

Fig. 4. CV curves at different potential scan domains of glassy carbon electrode for 0.5 mM of **L** in 0.1M TBAP/CH$_3$CN

Assigning of peaks appearing in voltammetric curves to specific reactions is difficult in the absence of laborious studies of the electrolysis products obtained at each potential. A documentary survey on the reduction of benzylidene rhodanine (which is similar to azulene rhodanine) shows that it is reduced at very negative potentials (this fact can be explained by the bulkiness of the trimethylazulene moiety that hinders electron transfer on the electrode). However, several peaks can be attributed, what is mostly due to different electron densities of the main components of the molecule. Therefore, the peak a1 represents formation of the radical cation, with positive charge being stabilized on the azulene seven-membered cycle as tropylium ion. The second peak a2 represents formation of higher reactive rhodanine radicals which marks the beginning of the polymerization process. In the cathodic domain it is expected that the vinylic double bond is reduced first at the potential of c1, and some desulfuration processes become active at the potential of c2. The reversible peak appearing at higher scan rates (d) at

the potential of -1.8 V at 0.5 V/s (Fig. 3A) could represent reduction of the C=O bond.

Table 1. Peak potential (V) values (vs. Fc/Fc$^+$) and process types for [**L**] = 0.5 mM in 0.1M TBAP/CH$_3$CN

Peak	Method		Process type
	DPV	CV	
a1	0.473	0.49	(i)*
a2	0.94	0.98	(i)*
a3	1.61	1.57	(i)*
c1	-1.54	-	(i)*
d	-	-1.62	(i)*
c2	-2.21	-2.11	(r)*
c2'	-	-1.93	

* r - reversible process; i - irreversible process

Fig. 5 presents RDE curves of glassy carbon electrode obtained at different rotation rates (500 – 1500 rpm) and DPV curve for 0.5mM of **L** in 0.1 M TBAP/CH$_3$CN. Three processes showing peaks in the anodic domain (a1, a2, a4) and two waves in the cathodic domain (c1 and c2) can be observed in Fig. 5A. They are denoted according to the notation given for the peaks of DPV curve shown in Fig.5B. The peculiar shape of RDE curves in the anodic scans is due to the formation of insulating polymer films that cover the electrode surface and lead to drop of the current to the baseline value. The peak a4 (seen in Fig. 2 on CV curves at different concentrations) could not be explained yet.
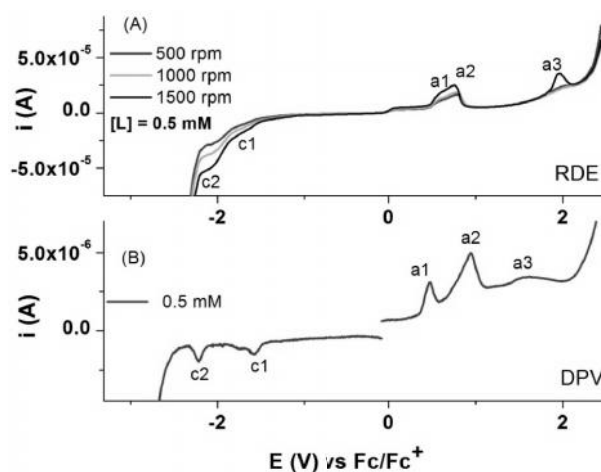

Fig. 5. (A) RDE curves (0.01 V/s) at different rotation rates (500 – 1500 rpm) and (B) DPV curves of glassy carbon electrode for 0.5 mM of **L** in 0.1 M TBAP/CH$_3$CN.

The current values from RDE curves increase with the rotation rate, more for the cathodic waves and less for the anodic processes. This behavior is also in agreement with the formation of insulating films in the anodic region of potentials.

Modified electrodes

PolyL modified electrodes have been prepared from 0.5 mM L in 0.1 M TBAP/CH₃CN by either successive potential scans, or by controlled potential electrolysis (CPE). The prepared modified electrodes were transferred into the ferrocene solution (1 mM) in 0.1M TBAP/CH₃CN. The ferrocene signal in CV curves of modified electrodes has been compared with the ferrocene signal on the bare electrode. CVs of two polyL modified electrodes obtained by 20 successive potential scans performed between −0.3V and two anodic limits of 0.6V and 1.12V, respectively, are shown in Figs. 6A and 6B.
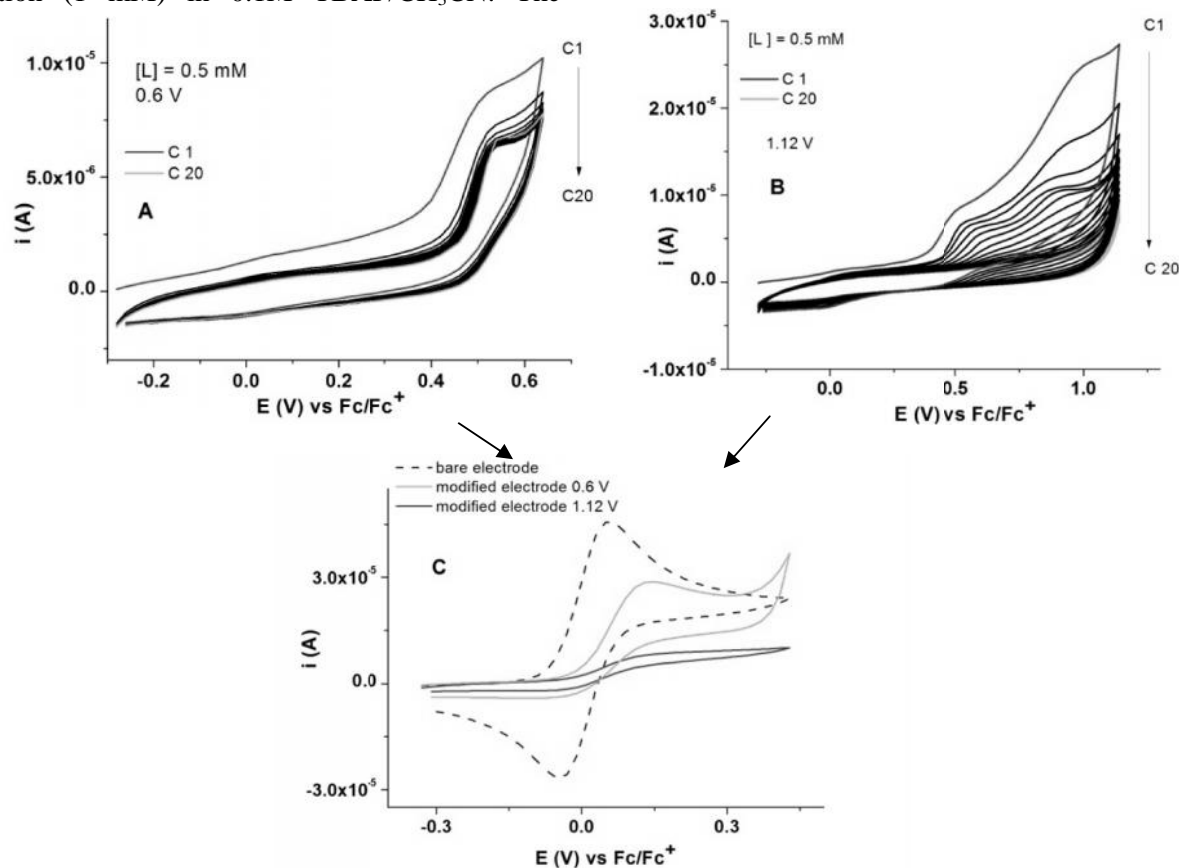

Fig. 6. CV curves (0.1 V/s) of polyL modified electrodes obtained by successive potential scanning between -0.3V and different anodic limits, 0.6 V (A) and 1.12 V (B) and the corresponding CV curves (0.1V/s) measured in 1mM ferrocene solution (C).

CV curves of these two modified electrodes in the ferrocene transfer solution are shown in Fig. 6C. It can be seen that the ferrocene signal is much more distorted for the polyL modified electrode prepared with the anodic limit of 1.12V. That is why this anodic limit of the potential was chosen to prepare modified electrodes by the potential cycling procedure, because the electrode is more covered with the polymeric film. This fact ensures a bigger amount of complexing units in view of complexation and leads to a better detection of heavy metals in our experiments.

The potential of 1.12 V has also been selected for polyL modified electrodes prepared by CPE (Fig. 7). At this potential value, different electropolymerization charges (0.5 and 1 mC) were used, and the CVs of CPE prepared modified electrodes are compared in Fig. 7.
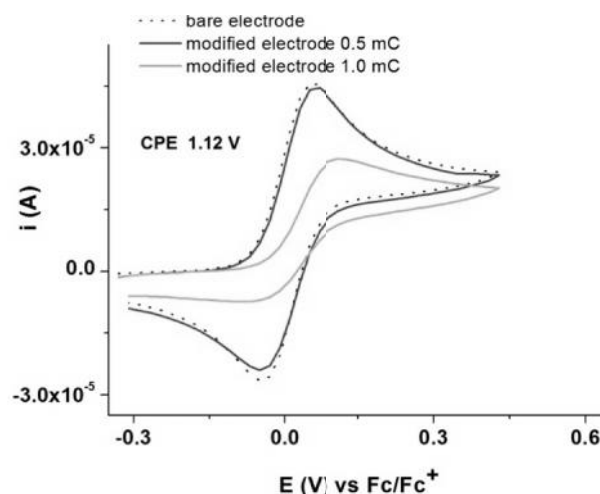

Fig. 7. CV (0.1 V/s) curves of polyL modified electrodes prepared by CPE at 1.12 V in 0.5 mM solution of L in 0.1M TBAP/CH₃CN using different electropolymerization charges and measured in 1 mM ferrocene solutions in 0.1M TBAP/CH₃CN.

The ferrocene signal for the modified electrode obtained at 1 mC is more flattened than that at 0.5 mC (which is close to that of the bare electrode). Since better coverage of the electrode occurs at higher charge, the poly**L** modified electrode obtained at 1 mC was chosen for the recognition experiments.

Evaluation of recognition properties

During the transition metals amperometric titration using p-dimethylaminobenzylidene rhodanine as titrant in 30% (vol) alcoholic dimethylformamide, the applied potential was varied with respect to the detected metal ions. The potential values were -0.50, -1.10, and -1.3V *vs.* SCE for Cu(II), Ni (II), Fe (II) and Zn(II), at pH 5.00 for Cu (II), 5.70 for Ni (II), 5.30 for Fe (II) and 5.05 for Zn (II), respectively. The end-point of the ligand titration indicated formation of complexes Me:L = 1:2. The error is under 1% and the detection is till 2×10^{-4} M [1].
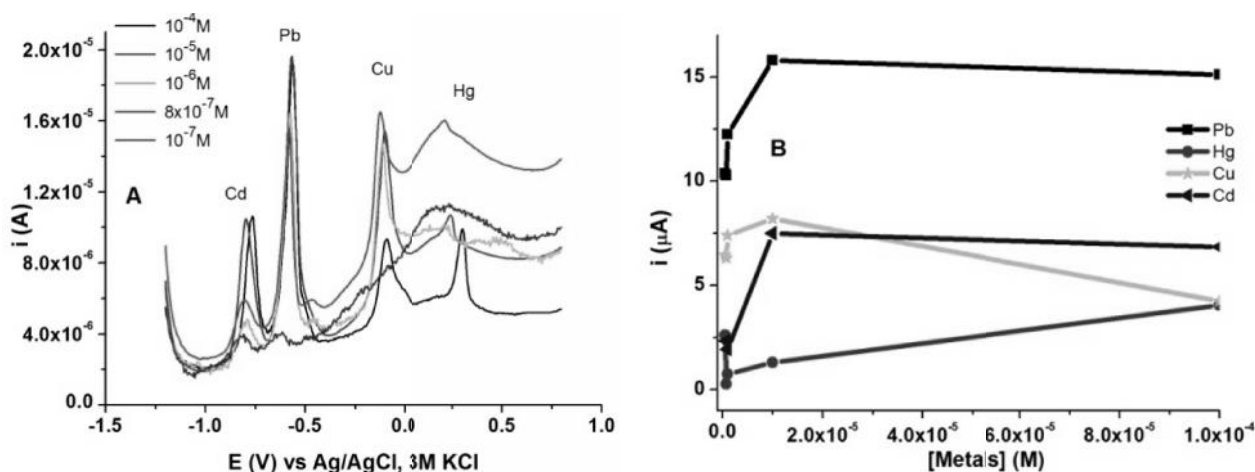
We tried to find another method for heavy metal determination that could monitor these metals at lower concentrations. For heavy metals recognition, poly**L** modified electrodes obtained by CPE (1.2V, 1mC) from the solution of **L** (1 mM) in 0.1M TBAP/CH_3CN have been used. After cleaning with acetonitrile, the modified electrodes were immersed in the transfer solution containing 0.1 M acetate buffer at pH 5.5. After 15 cycles of equilibration (by CV with a scan rate of 0.1 V/s between -0.9 V and +0.6 V) and overoxidation (by CV with a scan rate of 0.1 V/s between -0.2 V and +2.5 V), the modified electrodes were extracted from the cell, washed with water, and put in solutions containing heavy metals ions of different concentrations, under magnetic stirring for 15 minutes. Then, the modified electrodes were polarized at -1.2V, where all cations were reduced, and their DPV stripping currents were recorded between -1.2 V and 0.5V (Fig. 8A).

Fig. 8. DPV stripping currents for the poly**L** modified electrode obtained by CPE (1.12V,1mC) in 0.5 mM solution of L in 0.1M TBAP/CH_3CN, measured at different concentrations of heavy metals in acetate buffer at pH 5.5 (A) and DPV stripping currents in dependence on heavy metals concentration (B).

The calibration curves have been obtained for each heavy metal. The dependences of the DPV stripping currents on the heavy metals concentration are shown in Fig. 8, suggesting that the best analytical signals have been obtained for Pb.

CONCLUSIONS

(E)-2-thioxo-5-((4,6,8-trimethylazulen-1-yl)methylene)thiazolidin-4-one (L) has been studied by electrochemical methods. The study led to the finding of the best potential at which this azulene could be polymerized. PolyL modified electrodes were characterized by cyclic voltammetry in ferrocene solutions. The modified electrodes were used for heavy metals recognition

through preconcentration and anodic stripping. The best response has been obtained for Pb (detection limit of 10^{-7}M).

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(E)-2-thioxo-5-((4,6,8-trimethylazulen-1-yl)methylene)thiazolidin-4-one (**L**)

,

.   **L**

,   (Cd, Pb, Cu, Hg)   .

-   Pb (10^{-7}).