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Nanomolar determination of Pb(II) ions using a selective templated electrode

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Abstract: A polypyrrole-modified electrode, prepared by electro-polymerization of pyrrole in the presence of methyl red as a dopant, was templated with respect to Pb²⁺ and applied for the potentiometric and voltammetric detection of this ion. The templating process improved the analytical response characteristics of the electrode, especially its selectivity with respect to Pb²⁺. The improvement depended on both the incorporated ligand (dopant) and the templating process, with the latter being more vital. The potentiometric response of the electrode was linear within the Pb²⁺ concentration range of 2.0×10⁻⁶ to 5.0×10⁻² M with a near-Nernstian slope of 28.6 mV dec⁻¹ and a detection limit of 7.0×10⁻⁷ M. The electrode was also used for pre-concentration differential pulse anodic stripping voltammetry (DPASV) and the results showed that the peak currents for the incorporated lead species were dependent on the metal ion concentration in the range 1.0×10⁻⁸ to 1.0×10⁻³ M. The detection limit of the DPASV method was 3.5×10⁻⁹ M. The selectivity of the electrode with respect to some transition metal ions was investigated. The modified-templated electrode was used for the successful assay of lead in two standard reference material samples.

Keywords: templated polymers; lead; polypyrrole; potentiometry; voltammetry; nanomolar.

INTRODUCTION

Conducting polymers are very attractive due to their potential use as electrochromic devices, capacitors, gas separation membranes, anti-static membranes, catalysts, electromagnetic shielding devices and selective sensors.¹ The most important property of conducting polymers is their doping/imprinting ability with

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various molecular and ionic species. Therefore, various recognition elements can be introduced into these polymers during the polymerization step.^{2,3} Conducting polymers with specific affinities can be prepared in the presence of template molecules by chemical derivatization of the polymer with various compounds, or by doping the polymer with specific ligands.^{4,5} Among different conducting polymers, polypyrrole (PPy) has found attractive applications as one of the fundamental building materials in the design of various analytical tools because of its good stability, facile synthesis, higher conductivity and versatility.^{6,7} Following Dall'Olio *et al.* who initially deposited PPy by electrochemical polymerization of pyrrole from dilute sulfuric acid solution⁸ and Diaz *et al.* for electrochemically synthesizing the first free-standing PPy films,⁹ there has been an increasing interest in the application of electro-polymerized PPy for the development of various electrochemical sensors,¹⁰ including voltammetric^{11,12} and potentiometric^{13–15} sensors.

The increasing presence of toxic pollutants in the environment has been perceived as a major problem in the last decades.¹⁶ Modern medicine confirms that lead and its compounds are hazardous to people's nerve, blood, digestion, cardiovascular and other endocrine systems. Furthermore, unlike organic compounds, lead species are non-biodegradable that facily accumulate in soils and waters. Pb²⁺ is one of the most common ions assayed in environmental samples, and there is an increasing interest in its determination because of its toxicological effects.¹⁷

A wide range of analytical techniques are used for the detection of Pb²⁺ in various samples, including atomic absorption spectrometry (AAS), atomic emission spectroscopy (AES), inductively coupled plasma mass spectrometry (ICP-MS)^{18–21} and reflectance spectrometry.²² These techniques can offer good limits of detection and wide linear ranges, but are very expensive and require adequate expertise. Therefore, the analysis is often limited to laboratory level only. The need for rapid and in-field analysis of trace heavy metal ions is of tremendous interest in environmental applications. The electrochemical methods for determination of Pb²⁺ require instrumentation of relatively low cost and low maintenance.^{23–26} Using the differential pulse anodic stripping voltammetry (DPASV) technique, very low detection limits for many metal ions with wide linear ranges can be obtained.^{27,28}

Among different modified electrodes and electrochemical sensors,^{29,30} the technique of templating/imprinting polymers has shown considerable promise as a method of choice for preparing materials with the capability for recognition of molecules and ions.³¹ Such polymers, besides their ease of production, low cost and stability in harsh environments, show high affinity and selectivity to the target species.³²

In this study, the templating approach was used to develop a templated PPy-based sensor for potentiometric and voltammetric determination of Pb²⁺. The

method is based on the application of successive potential steps to the electropolymerized Methyl Red/PPy film (MR/PPy) in $\text{Pb}(\text{NO}_3)_2$ as the only electrolyte present in solution. During these steps, the membrane is templated with respect to Pb^{2+} . The resulting sensor exhibited a noticeable enhancement in the potentiometric and voltammetric response characteristics, extending the linear dynamic range and lowering the detection limit.

EXPERIMENTAL

Materials

Methyl Red (MR), potassium nitrate (KNO_3), lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$) and nitrate salts of all other cations were purchased from Merck and used without further purification. Pyrrole monomer (Fluka) was purified by distillation under reduced pressure and stored at a low temperature protected from light. The pH adjustment was made with dilute nitric acid and sodium hydroxide solutions as appropriate. Doubly distilled water was used throughout.

Apparatus

The electropolymerization and all the voltammetric measurements were performed using a potentiostat/galvanostat Autolab (model PGSTAT 302 N). A conventional three electrode cell, including a glassy carbon (GC) disk electrode of 2 mm diameter (Azar Electrode, Uromieh, Iran) modified with MR/PPy film (MR/PPy/GC) as the working electrode, a saturated double salt bridge $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$ (SCE) from Metrohm as the reference electrode and a platinum wire (Metrohm) as the counter electrode, was used in the voltammetric experiments. The potential and pH measurements were performed on a pH/mV meter (Metrohm model 691). The MR/PPy/GC and SCE were used as indicator and references electrodes, respectively in the potentiometric measurements. All the potentials are quoted *versus* the reference electrode (SCE).

PPy Film electrode preparation

The GC disk working electrodes were polished with 0.3 μm alumina slurry and cleaned thoroughly with water. The electro-polymerization of PPy was performed from a deoxygenated aqueous solution containing 0.1 M pyrrole and 1.0×10^{-4} M Methyl Red on the polished GC surface using the potentiostatic method by application of a potential of +0.75 V for the desired period under an atmosphere of pure argon.

After the electro-polymerization, the electrode was washed with water and then subjected to several alternative reduction/oxidation steps in a solution containing 1.0×10^{-3} M $\text{Pb}(\text{NO}_3)_2$. The reduction and oxidation steps were performed potentiostatically at -0.4 and 0.5 V, respectively, each for a period of 5 min. The overall process was repeated three times, followed with an oxidation step for a period of 10 min. The prepared MR/PPy/GC electrode was then directly used for voltammetric measurement or conditioned in 1.0×10^{-3} M $\text{Pb}(\text{NO}_3)_2$ solution for at least 19 h prior to its use as the indicator electrodes for potentiometric measurements.

Potentiometric measurements

The MR/PPy/GC was used as the indicator electrode in conjunction with an SCE reference electrode. The analytical performance of the electrode was investigated by measuring its potential response in Pb^{2+} solutions, freshly prepared in the concentration range of 1.0×10^{-9} to 0.10 M by serial dilution of a stock 0.10 M solution of this salt. The solution was stirred

and the potential was recorded when it attained a stable value. The data were plotted as the observed potential vs. the logarithm of the Pb^{2+} activity to construct a calibration plot.

DPASV Measurements

The voltammetric measurements were carried out using the modified MR/PPy/GC as the working electrode together with the reference and counter electrodes. The pre-concentration step was carried out by dipping the electrodes in the sample solution and applying a potential of -0.7 V vs. SCE for a period of 200 s. Then the electrode was washed with water and transferred to a cell containing 0.2 M potassium nitrate electrolyte solution at pH 2.0. The DPASV was performed in the potential range of -0.9 to -0.1 V at a scan rate of 100 mV s^{-1} .

Sample pretreatment

Two standard reference materials (SY-4, a CANMET standard rock and SGHM-2 (3484-86), an aluminous silicate standard from Institute of Geochemistry SB RAS, Irkutsk) were used for real sample analysis. The following procedure was used for pretreatment of these samples. To 0.3 g of each sample was added 25 mL of 2.0 M nitric acid and the resulting solution was heated for 3 h at 60 °C. Then the solution was filtered through a filter paper, neutralized with sodium hydroxide solution to pH 5.6 and after dilution to 100 mL, used for the voltammetric measurements.

RESULTS AND DISCUSSION

Electropolymerization of pyrrole and the templating process

A PPy film with incorporated Methyl Red was formed on the surface of a GC electrode from an aqueous solution containing 0.10 M pyrrole monomer and 1.0×10^{-4} M Methyl Red by using a constant potential of 0.75 V. During the electropolymerization, pyrrole was first oxidized to give the corresponding radical cations, followed by a coupling reaction to give oligomers and finally polymer on the electrode surface.

After the electro-polymerization step, the electrode was washed with water and transferred to a cell containing 1.0×10^{-3} M $\text{Pb}(\text{NO}_3)_2$, the only electrolyte present in solution, for the templating process. Then the electrode was subjected to three redox potential steps in this solution, as described in the experimental section. During these steps, the polymer backbone underwent successive reduction/oxidation reactions, resulting in generation of neutral/positively charged PPy chains, accordingly. During the reduction step, the polymer backbone became neutral, making the MR/PPy membrane negatively charged. Under this condition, Pb^{2+} present in solution was incorporated into the polymer. When the polymer was re-oxidized, the MR/PPy film became neutral and the incorporated metal species were expelled from the membrane. The templating process was found to be essential for obtaining high selectivity and better response characteristics in both potentiometric and voltammetric measurements.

Optimizing the electropolymerization and pre-concentration conditions

The voltammetric response characteristics of the modified electrodes strongly depended on the electropolymerization conditions. Therefore, the DPASV peak height was used as the criterion for selecting the optimum operating conditions in the electropolymerization process. The influence of various electropolymerization parameters and conditions, including the pyrrole and Methyl Red concentrations, the pH of the solution and polymerization charge or membrane thickness, were investigated.

The DPASV peak current depended on both the pyrrole and Methyl Red concentrations. Maximum response was observed for 0.10 M pyrrole and 1.0×10^{-4} M Methyl Red concentrations. The influence of pH of the electro-polymerization solution on the DPASV signal is shown in Fig. 1. As can be seen, the peak current increased with increasing pH of the solution up to 5.7 and then decreased slowly for higher pH values. Methyl Red is protonated at low pH values but is in anionic form at pH values higher than 5 (the pK_a of MR is 5.1), therefore MR can be incorporated into the PPy because of its anionic charge and the DPASV signal increased at pH values higher than 5. Since the pH of the polymerization solution containing 0.10 M pyrrole and 1.0×10^{-4} M MR was 5.6, there was no need to adjusting the solution pH.

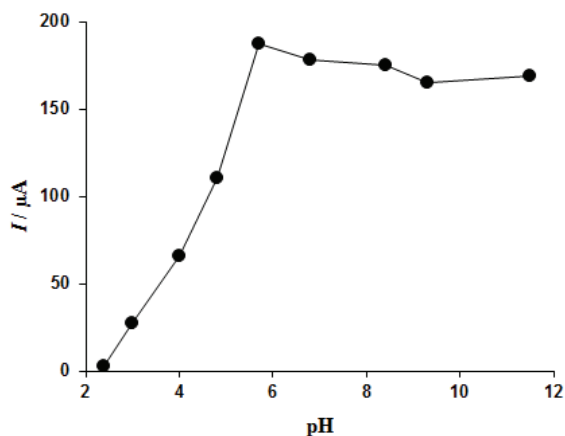


Fig. 1. Influence of pH of electro-polymerization solution on the DPASV signal.

The voltammetric response of the MR/PPy film electrode, expressed as the DPASV peak height, was influenced by the film thickness, which can be controlled by the polymerization time. It was found that maximum DPASV signal was observed when the polymerization time was 30 s. At films thinner than this (shorter polymerization time), the DPASV peak current decreased sharply, because there is not enough binding sites on the electrode for interaction with Pb^{2+} . Thicker films (longer polymerization time) increase the electrode resistance and

pose mass transfer limitations to Pb^{2+} , during the accumulation and stripping steps, and thus, lower the sensitivity of the measurement.

The influence of the pre-concentration conditions was also investigated by varying the pH, applied potential and pre-concentration time for a 1.0×10^{-5} M Pb^{2+} solution (Fig. 2). The effect of pH on the pre-concentration of Pb^{2+} into the modified electrode was investigated by varying pH between 1.5 and 13 and measuring the DPASV signal. The results showed that the peak current was almost independent of pH in the range of 5.0–9.1, as shown in Fig. 2A. Interference from H^+ due to protonation of the coordination sites of the membrane at low pH values and the formation of insoluble species at high pH values are possible reasons for lower DPASV signal in these regions.

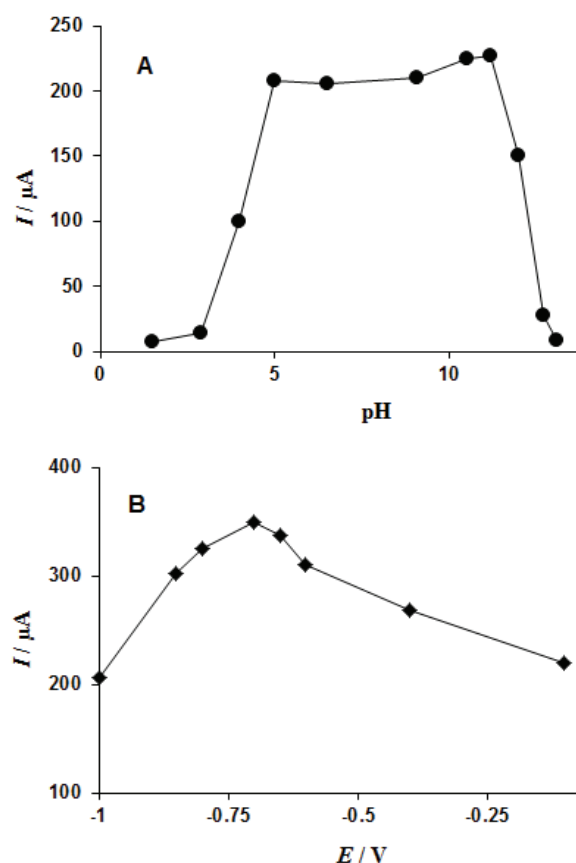


Fig. 2. Influence of the pre-concentration conditions on the DPASV signal; A) pH of the pre-concentration solution and B) applied pre-concentration potential.

Pre-concentration of lead species into the MR/PPy film strongly depended on the applied potential, as shown in Fig. 2B. The maximum DPASV signal was observed at an applied pre-concentration potential of -0.7 V. The reason for the lower efficiency at potentials more positive than -0.7 V is the incomplete reduc-

tion of PPy and consequently reduced pre-concentration of lead species into the membrane. Lower efficiency at potentials more negative than -0.7 V can be related to reduction of the azo group in Methyl Red and cleavage of the N=N bond of this compound.³³ The pre-concentration time depended on the concentration of Pb^{2+} , however, a 200 s period was determined to be sufficient for all the studied concentrations and no further improvement could be observed after this period.

Voltammetric response of the electrode

Voltammetric calibration. The modified-templated electrode was used for pre-concentration/DPASV measurement of Pb^{2+} . At the optimized conditions, the DPASV measurements were performed by transferring the electrode, after pre-concentration, into a cell containing 0.20 M potassium nitrate adjusted to pH 2.0, and scanning the potential from -0.9 to -0.1 V using a pulse amplitude of 50 mV and a scan rate of 100 mV s^{-1} . The DPASV peak current was dependent on log of the Pb^{2+} concentration over a wide concentration range of 1.0×10^{-8} to 1.0×10^{-3} M with a slope of $32.54 \mu\text{A}/\log c_{\text{Pb}^{2+}} (\text{mol/l})$ and $R^2 = 0.992$, as shown by the calibration plot in Fig. 3. The RSD of DPASV for 5.0×10^{-7} M Pb^{2+} peak current was 5.1 % ($n = 7$) and the detection limit was determined to be 3.5×10^{-9} M Pb^{2+} .

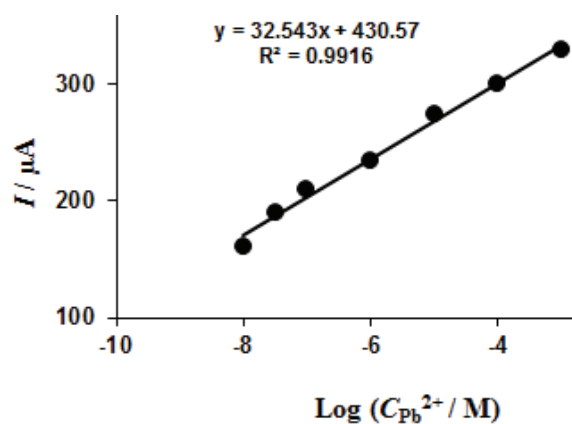


Fig. 3. Voltammetric calibration curve for the modified-templated electrode under the optimum conditions.

Interference study

Interference studies of several cationic species on the DPASV of Pb^{2+} were performed in mixture experiments. Pre-concentration was performed in solutions containing 1.0×10^{-5} M Pb^{2+} and different concentrations of interfering ions at a potential of -0.7 V for a period of 200 s and then DPASV was performed as usual. The results indicated that most of the ions did not interfere significantly; however, interference of Cu^{2+} was considerable.

Potentiometric response of the electrode

Before the potentiometric measurements, the modified-templated electrode was conditioned in 1.0×10^{-3} M lead(II) nitrate solution. After conditioning for approximately 19 h, a stable Nernstian response was obtained for Pb^{2+} solutions of various concentrations. To test the performance of the electrode characteristics, various operation parameters, such as working concentration range, selectivity, and the effect pH were investigated.

Effect of pH

The effect of the pH of the test solution on the potentiometric response of the templated electrode was examined in a 1.0×10^{-5} M Pb^{2+} solution adjusted to different pH values with dilute nitric acid or sodium hydroxide solutions. As illustrated in Fig. 4, the electrode can be used in the pH range of 5.2–10. A substantial increasing trend in the potential was observed at $\text{pH} < 5.2$, which may be due to participation of H^+ in the ion exchange processes on the polymer/solution interface.³⁴ The potential drop at high pH values (>10) may be because of precipitation of Pb^{2+} .

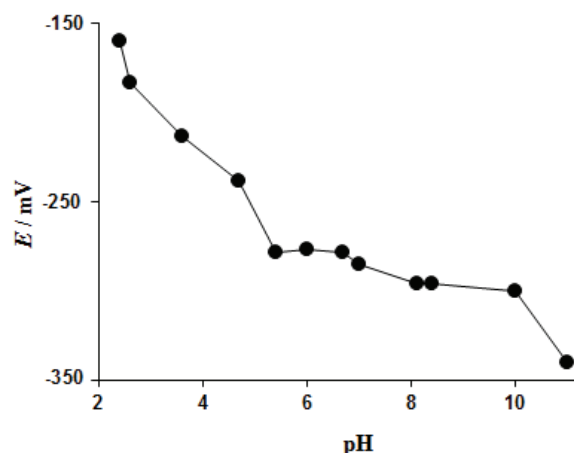


Fig. 4. Effect of the pH of the test solution on the potentiometric response of the templated electrode at 1.0×10^{-5} M Pb^{2+} solution.

Potentiometric calibration

The potentiometric response of the electrode was investigated in solutions of different Pb^{2+} concentrations at pH 5.6. The calibration plot of the electrode is shown in Fig. 5, indicating a linear response over the concentration range of 2.0×10^{-6} to 5.0×10^{-2} M with a Nernstian slope of 28.6 mV per decade of Pb^{2+} activity. The detection limit was 7.0×10^{-7} M Pb^{2+} . Comparison between the potentiometric response of the templated and untemplated electrodes, indicated a much improved sensitivity, dynamic range and detection limit for the templated electrode.

Potentiometric selectivity coefficient

The potentiometric selectivity of the templated and untemplated modified electrodes were studied by the separate solution method (SSM), according to IUPAC recommendations,³⁵ using 1.0×10^{-3} M Pb^{2+} and interfering ions. From the selectivity coefficients summarized in Table I, it is obvious that most of the metal ions examined on the templated electrode did not show obvious interferences in the determination of Pb^{2+} . However, copper ion showed a significant interference. The untemplated electrode showed lower selectivity for Pb^{2+} with respect to all of these ions. According to the results of Table I, the templating step has an important role in generating recognition sites for Pb^{2+} .

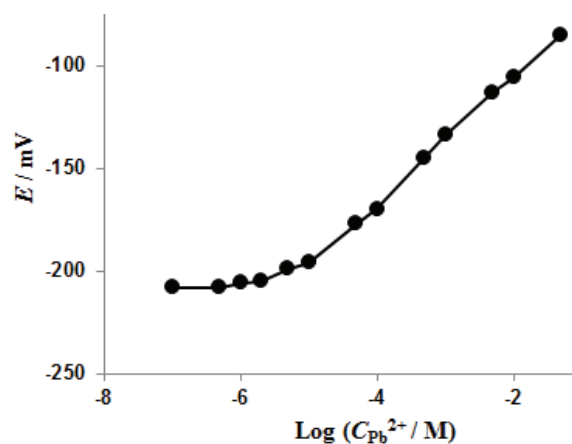


Fig. 5. Potentiometric calibration curve of the modified-templated electrode at pH 5.6.

TABLE I. Selectivity coefficients ($\log K_{\text{Pb}^{2+}, \text{M}^{n+}}$) of the modified electrode for Pb^{2+} with respect to some other ions

Ion	Before templating	After templating
Cr^{3+}	-1.79	-2.27
Fe^{2+}	-3.16	-4.00
Ag^+	-3.76	-3.80
K^+	-1.37	-2.71
Cd^{2+}	-0.31	-3.74
Mg^{2+}	0.338	-0.135
Ca^{2+}	1.86	-0.96
Na^+	0.10	-0.72
Mn^{2+}	0.45	-0.24

Analytical application

The templated electrode was applied for the determination of the lead content in two standard ore samples by the voltammetric method and the results were compared with the certified concentration of lead in these samples (Table II). The samples were prepared as described in the Experimental section. The re-

sults show that, in spite of the presence of high concentrations of different components, including alkaline and alkaline earths, and significant concentrations of various transition elements in these samples, there was a good agreement between the certified and measured concentrations of lead, indicating the capability of the modified electrode for the determination of lead in real samples.

TABLE II. Application of the electrode for the determination of the lead content ($\mu\text{g g}^{-1}$) of standard ore samples by DPASV, comparison between the determined and certified concentrations

Sample	Certified value	Found value ($n = 4$)
SY-4	10 \pm 1	10.9 \pm 1.0
3484-86 (SGHM-2)	1.6 $\times 10^{-3} \pm 3.0 \times 10^{-4}$	1.8 $\times 10^{-3} \pm 2.9 \times 10^{-4}$

CONCLUSIONS

The electrode modified with MR/PPy was studied as a potentiometric and voltammetric sensor for Pb^{2+} . The results indicated that the templating process performed by applying a potential step program to the electropolymerized MR/PPy membrane in a solution containing $\text{Pb}(\text{NO}_3)_2$ as the electrolyte improved the selectivity of the electrodes toward the Pb^{2+} ion. This process seems to rearrange the binding sites of both the PPy and the ligand, and therefore, generates chemical recognition elements in the modified polymer film. The proposed sensor was successfully applied for the measurement of Pb^{2+} using potentiometry in the range of 2.0×10^{-6} to 5.0×10^{-2} M and DPASV in the range of 1.0×10^{-8} to 1.0×10^{-3} M, with improved selectivity compared to the untemplated electrodes. It seems that by judicious selection of the chelating ligand and change of the polymerization and templating factors, it may be possible to induce better selectivity for Pb^{2+} and to extend this approach to other cationic species.

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ИЗВОД

ОДРЕЂИВАЊЕ Рb(II) ЈОНА У НАНОМОЛАРНОМ РАСТВОРУ ПОМОЋУ ПОЛИМЕРНЕ ЕЛЕКТРОДЕ СА ПРЕТХОДНО ДЕФИНИСАНОМ СЕЛЕКТИВНОШЋУ

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Електрода која је претходно модификована електрополимеризацијом полипирола уз метиленско црвено као допант, додатно је електрохемијски допована/депована јонима Pb^{2+} , чиме јој је дефинисана селективност, а затим коришћена за потенциометријску и волта-

метријску детекцију поменутих јона. Процес електрохемијског доповања/дедуповања побољшао је аналитичке карактеристике електроде, посебно њену селективност према Pb^{2+} . Степен побољшања зависи и од укљученог лиганда (допанта) и од електрохемијског доповања/дедуповања, при чему је други фактор значајнији. Потенциометријски одговор електроде је био линеаран у опсегу концентрације од $2,0 \times 10^{-6}$ to $5,0 \times 10^{-2}$ M са нагибом од 28,6 mV дек⁻¹, као што предвиђа Нернстова једначина, и границом детекције од $7,0 \times 10^{-7}$ M. Електрода је такође коришћена за диференцијалну пулсну анодну стрипинг волтаметрију (ДПАСВ) уз претходно укључивање олова из испитиваног раствора у полимерни филм. Резултати су показали да струја максимума зависи од концентрације металних јона у опсегу од $1,0 \times 10^{-8}$ до $1,0 \times 10^{-3}$ M. Граница детекције методе ДПАСВ је $3,5 \times 10^{-9}$ M. Испитивана је и селективност електроде у односу на поједине јоне прелазних метала. Модификована допована/дедупована електрода је успешно тестирана за одређивање олова у два стандардна референтна узорка.

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