

Voltammetric Detection of Mercury(II) Using Lead Powder-Modified Thiol-Functionalized Polysiloxane Film Electrode

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Abstract: Surfactant-templated silica films functionalized with thiol groups and modified with lead powder have been deposited during one-step process onto glassy carbon electrodes. This strategy was based on co-condensation of tetraethoxysilane and 3-mercaptopropyltrimethoxysilane in the presence of cetyltrimethylammonium bromide, and modification of sol by the appropriate amount of lead powder. After template extraction, the novel lead powder modified thiol-functionalized polysiloxane film electrode was applied to the determination of Hg(II). The obtained results indicated that the sensitivity at this electrode was remarkably improved with relative to the thiol-functionalized polysiloxane film electrode prepared without use of the lead powder. Various parameters have been optimized to get the highest current response, such as the film composition, accumulation time, detection conditions, and concentration of analyte. Linear calibration curve was obtained in the Hg(II) concentration range from 5×10^{-8} to 1×10^{-5} mol L⁻¹ for the accumulation time of 60 s. The detection limit estimated from 3 times the standard deviation for the lowest determined concentration of Hg(II) was equal to 1.9×10^{-8} mol L⁻¹. It has to be noted, that the detection limit can easily be improved by the prolongation of the accumulation time up to 30 min.

Keywords: Lead powder; Thiol-functionalized polysiloxane film; Modified electrodes; Hg(II) detection.

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Introduction

Chemical modification of electrode surfaces is a well-established strategy for improving the analytical performance of conventional electrode materials for specific applications in various fields [1], and especially electroanalysis and sensors [2,3]. Among the wide range of materials that have been used for electrode modification, those based on silica display several interesting properties: high specific surface area, reactive surface silanol groups, mild conditions for their preparation via sol-gel process, and possibility of chemical modification by numerous (bio-)organic groups [4,5].

The usual way to get organic-inorganic hybrid silica films (functionalized polysiloxane films) onto solid substrates is the so-called “evaporation-induced self-assembly” (EISA) process [6-9]. In a typical EISA synthesis, a sol containing the sol-gel precursors along with an appropriate template component (i.e., cetyltrimethylammonium bromide (CTAB)) is cast over the surface of the substrate and film formation is driven by solvent evaporation; an accurate control of experimental conditions (i.e., sol composition, humidity, evaporation rate) enables fine tuning of the resulting mesostructure type (2D- or 3D-hexagonal, cubic, lamellar, etc) [6,8]. Extraction of the surfactant (template component) from functionalized polysiloxane films leads to a large increase of mass transport rates into materials and imported high accessibility to the organic moieties of organofunctionalized porous overlayers. Interestingly, the templating approach prevents the appearance of cracks into the film, even after surfactant removal [10].

The mesoporous organosilica modified electrodes were particularly applied to the determination of heavy metals species. The thiol-functionalized mesoporous silica was used in the modification of carbon paste electrode for Hg(II) and Pb(II) detection [11-14], in thin film electrode for determination of Ag(I) [15] and in screen-printed carbon electrodes for Eu(III) and Hg(II) detection [16,17]. Additionally, Cu(II) sensing using oriented mesoporous silica films bearing aminopropyl groups was reported [18]. Recently, 5-mercaptopropyl-1-methyl-1H-tetrazole (MTTZ) functionalized silica films on glassy carbon electrode was used to the determination of Hg(II) [19].

In this work, we have prepared surfactant-templated thiol-functionalized silica films modified with lead powder on a glassy carbon electrode, via a one-pot EISA process by co-condensation of tetraethoxysilane and 3-mercaptopropyltrimethoxysilane in the presence of cetyltrimethylammonium bromide. The sol was modified by the appropriate amount of lead powder, before deposition on the electrode surface. After template extraction, the novel lead

powder modified thiol-functionalized polysiloxane film electrode was applied to the determination of Hg(II) (chosen as model analyte) in acidic medium, according to a two-step procedure (voltammetric detection after open-circuit accumulation). The influence of various factors likely to affect both the accumulation and detection steps has been investigated. In the present study we tried to point out the advantages of using the lead powder as the modifier of thiol-functionalized silica film electrodes.

Experimental

Chemicals and Reagents

All the solutions were prepared with water purified in Millipore Milli-Q system. The chemicals were of the analytical grade and used without further purification. Tetraethoxysilane 95 % (TEOS, Trimen), 3-mercaptopropyltrimethoxysilane 85 % (MPTMS, Trimen), cetyltrimethylammonium bromide 98 % (CTAB, Fluka), ethanol 99,8 % (Sigma-Aldrich), and HCl 37 % (Fluka) were used for the preparation of sol solutions. The lead powder (200 mesh, 99.9 %) for preparation of the modified polysiloxane films was purchased from Alfa Aesar – A Johnson Matthey Company (USA). A standard solution of Hg(II) (1 g L^{-1} , Merck) was used for the preparation of the working mercury solutions in 2 mol L^{-1} HNO_3 (Sigma-Aldrich).

Apparatus

All voltammetric measurements were performed using a μ Autolab analyser made by Eco Chemie, the Netherlands. A classical three-electrode quartz cell of volume 10 mL was used throughout, consisting of modified or unmodified glassy carbon working electrode, with an Ag/AgCl reference electrode and a platinum wire as an auxiliary electrode. The glassy carbon electrode was polished successively on silicon carbide paper (SiC-paper, #4000, Buehler, Denmark) and alumina particles suspension ($1 \text{ }\mu\text{m}$, $0.3 \text{ }\mu\text{m}$ and $0.05 \text{ }\mu\text{m}$) on a Buehler polishing pad and then was washed and sonicated for 2 min. In order to cast an adherent, reproducible and uniform film a glassy carbon electrode was first electrochemically activated according to the procedure earlier described in literature [20]. A polished and clean glassy carbon electrode was immersed into a 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) and its

potential was held for 45 s at +1.55 V followed by 45 s at -1.55 V. Finally, the potential was cycled between 0.5 V and -1.5 V until a reproducible cyclic voltammogram was obtained. A mechanical stirrer (type RZR 2021, Heidolph, Germany) was used to rotate electrodes during deposition of the polysiloxane films.

Preparation of a Lead Powder Modified Thiol-Functionalized Polysiloxane Film Electrode

The organosilica films modified with lead powder were deposited by spin-coating sol solutions on the freshly polished and electrochemically activated surface of a glassy carbon electrode. The sol solutions were prepared by adapting a procedure described by Zhao et al. [21]. These sols were obtained by heating a mixture of 0.93 g TEOS (including selected equivalent fractions (up to 40 %) of MPMTS), 2.75 g EtOH, and 0.2 g of an aqueous of HCl (0.1 mol L^{-1}) at $70 \text{ }^\circ\text{C}$ for 1 h, to which 0.39 g of CTAB dissolved in 5 g of EtOH was then added and stirred for 1 h at room temperature. Then, the polymeric silica sols were modified by adding lead powder (from 0.025 to 0.5 g per 10 mL of sol).

20 μL of sol from stirring solution was deposited on the electrode surface, and left 30 s before the electrode was rotated at 2000 rpm for 120 s. The spin-coated films were then aged at $100 \text{ }^\circ\text{C}$ for 30 min. Extraction of the surfactant template was performed in ethanol under hydrodynamic conditions (by rotating the electrode at 150 rpm) for 5 min. The film electrodes were used in the electrochemical experiments without further treatment.

Procedure of Mercury(II) Determination

A typical measurements of Hg(II) involves two successive steps: a glassy carbon electrode coated with a lead powder modified polysiloxane films containing 10 % of mercaptopropyl (thiol) groups was first immersed into the stirring accumulation medium (10 mL of solution of 0.1 mol L^{-1} HNO_3 containing appropriate concentration of Hg(II)) for 60 s. Then, the electrode was removed at the end of the preconcentration step, rinsed with deionized water and finally transferred into a working solution containing 3 mol L^{-1} HCl where detection was performed by anodic stripping voltammetry. In the detection medium the previously accumulated Hg(II) species complexed by the thiol groups are then directly reduced at -0.7 V during 300 s prior to be quantified by a square wave anodic scan from -0.25 to 0.3 V (vs. Ag/AgCl). The best results were obtained under the following conditions: frequency 25 Hz, step height 4 mV, and amplitude 25 mV.

Results and Discussion

The aim of this paper was the application of lead powder as a modifier of thiol-functionalized polysiloxane films in order to improve the electrochemical properties of organosilica modified film electrodes. Due to this fact, the amount of lead powder in the films was optimized. Additionally, parameters such as accumulation time, electrolysis potential and different quantities of MPTM, which influenced the voltammetric peak current of Hg(II), were optimized and discussed. It has to be noted, that the accumulation solution ($0.1 \text{ mol L}^{-1} \text{ HNO}_3$) and the detection solution ($3 \text{ mol L}^{-1} \text{ HCl}$) were used in all bellow experiments, according to the date described in literature [13,14]. It is well know that mercury forms stable complexes with chloride. However, it is possible that the stability of the thiol-functionalized polysiloxane complexes must be higher than those of chloride complexes with mercury [14], so a solution of HCl at concentration of 3 mol L^{-1} can be used as a supporting electrolyte to the detection of Hg(II).

Factors Affecting Preconcentration Process

Film Composition. Since an in situ plated lead film electrode was successfully introduced to electrochemical stripping analysis [22], other types and variations of this sensor are attracting continuous attention. The lead powder-modified thiol-functionalized polysiloxane film electrode represents a novel type of lead-based electrodes prepared by mixing of lead powder with organosilica sol. The composition and particularly the metal powder content can play an important role and influences the electroanalytical response of the electrode itself. Therefore the comparison of electroanalytical performance of the six thiol-functionalized polysiloxane film electrodes modified with different amount of lead powder was investigated in the first place. The content of lead powder in the polysiloxane sol was changed in the range from 0 to 50 g L^{-1} . The experiments were performed for Hg(II) concentration of $5 \times 10^{-7} \text{ mol L}^{-1}$. It was found that all six electrodes exhibited well-defined and sharp voltammetric stripping signals for mercury in $3 \text{ mol L}^{-1} \text{ HCl}$. However, the mercury peak current increases as the amount of lead powder added to the polysiloxane sol increases to $0.1 \text{ g}/10 \text{ mL}$ (10 g L^{-1}), so for further study this amount was chosen. Fig. 1 shows the anodic stripping voltammograms obtained at a bare glassy carbon electrode and the modified with selected content of lead (10 g L^{-1}) and unmodified thiol-functionalized polysiloxane film electrodes. As can be seen, the stripping voltammogram recorded at the lead powder-modified thiol-functionalized

polysiloxane film electrode displays higher signal for tested metal compared to the thiol-functionalized polysiloxane film electrode ($1.52 \mu\text{A}$ versus $0.63 \mu\text{A}$, respectively). It must be noted that at a bare glassy carbon electrode no oxidation peak of mercury was recorded. The above experimental results indicate the advantages of using lead powder as a modifier of a thiol-functionalized polysiloxane film electrode, so such prepared electrode was used in further measurements. The increase of the peak current of Hg(II) with the modification of thiol-functionalized polysiloxane film using lead powder probably is connected with the increase the active surface area of electrode. It will be subject of further study.

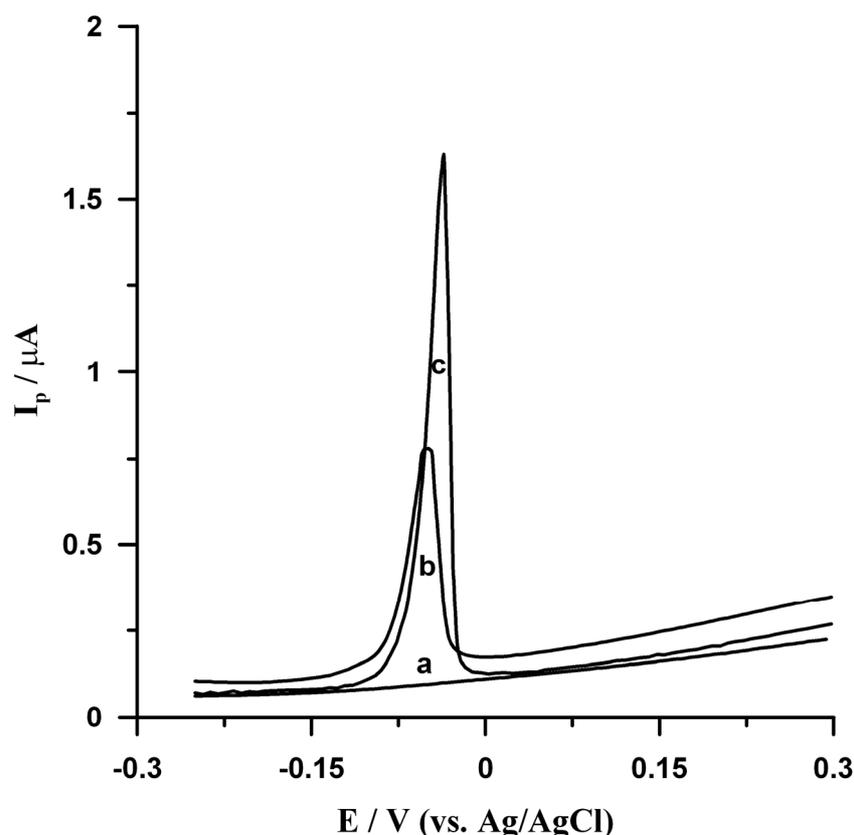


Fig. 1: Square wave anodic stripping voltammograms obtained in the course of the determination of Hg(II) at concentration of $5 \times 10^{-7} \text{ mol L}^{-1}$ at different electrodes. Legend: a) a bare glassy carbon electrode, b) the thiol-functionalized polysiloxane film electrode, c) the lead powder-modified thiol-functionalized polysiloxane film. Experimental conditions: preconcentration solution: $0.1 \text{ mol L}^{-1} \text{ HNO}_3$; deposition solution: $3 \text{ mol L}^{-1} \text{ HCl}$; accumulation time: 10 min.; amount of MPTMS in the starting sol: 10%, content of lead powder in sol: 10 g L^{-1} ; SWASV: electrolysis potential: -0.7 V vs. ref., electrolysis time: 60 s, frequency: 25 Hz, step height: 4 mV, and amplitude: 25 mV (for other details, see *Experimental*).

The effect of films containing different proportions of MPTMS (MPTMS/(MPTMS+TEOS) ratio in the starting sol) in the voltammetric response of the lead powder-modified thiol-functionalized polysiloxane film electrode was evaluated by square wave anodic stripping voltammetry of $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Hg(II)}$. The obtained results are presented in Fig. 2. As can be seen, the anodic peak currents of mercury increased with the amount of MPTMS in the film up to 10 % and decreased when more than 10 % MPTMS is used in the sol-gel preparation. According to these results a glassy carbon electrode covered with polysiloxane film containing 10 % of thiol groups and modified with lead powder was used in further experiments. Additionally, comparison between the peak current of mercury obtained for silica films prepared with (10 % of thiol groups) and without MPTMS ($1.52 \mu\text{A}$ versus $0.05 \mu\text{A}$, respectively) clearly demonstrates that the Hg(II) binding process is preferably due to complexation to the incorporated ligands (thiol groups) than surface silanol groups.

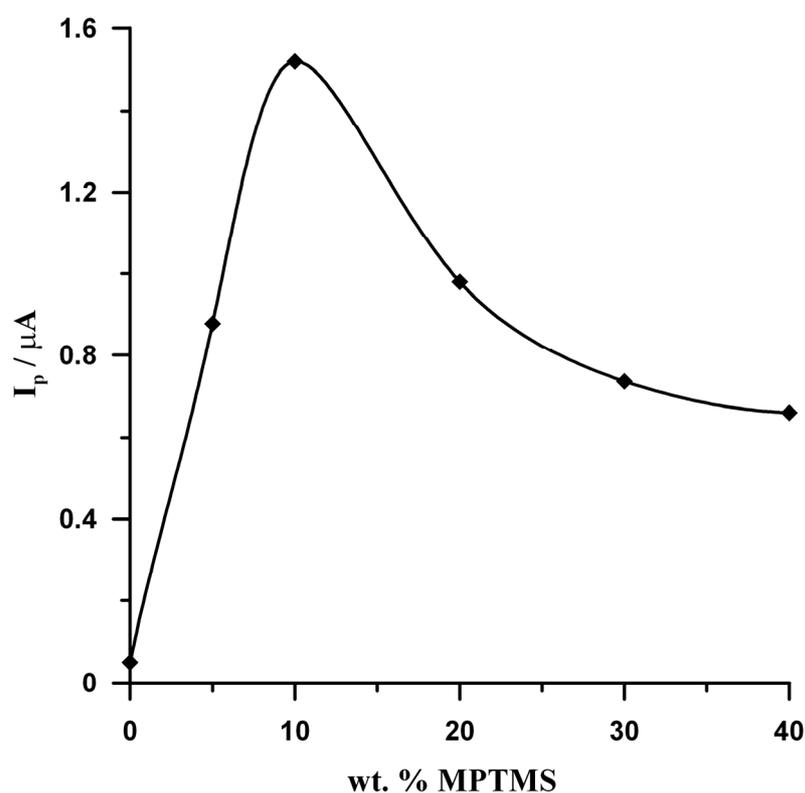


Fig. 2: Effect of the amount of MPTMS in the starting sol on the peak current of Hg(II) at concentration of $5 \times 10^{-7} \text{ mol L}^{-1}$. The glassy carbon electrodes were covered with MPTMS-functionalized silica film modified with lead powder from the same sol composition but by varying the MPTMS/(MPTMS+TEOS) ratio from 0.05 (5 %) to 0.40 (40 %). Experimental conditions: content of lead powder in sol: 10 g L^{-1} ; accumulation time: 10 min.; SWASV: electrolysis potential: -0.7 V vs. ref., electrolysis time: 60 s, frequency: 25 Hz, step height: 4 mV, and amplitude: 25 mV (other conditions as in Fig. 1).

Accumulation Time. Another important parameter likely to influence the preconcentration process is the accumulation time. The experiments were for Hg(II) concentration of $1 \times 10^{-6} \text{ mol L}^{-1}$. The influence of the accumulation time on the stripping peak currents is illustrated in Fig. 3. As expected, the oxidation peak currents of mercury were higher intensities at longer accumulation time as a result of larger amounts of accumulated species but this trend tended to level off. It can be explained by saturation of the binding sites in the polysiloxane film modified with lead powder.

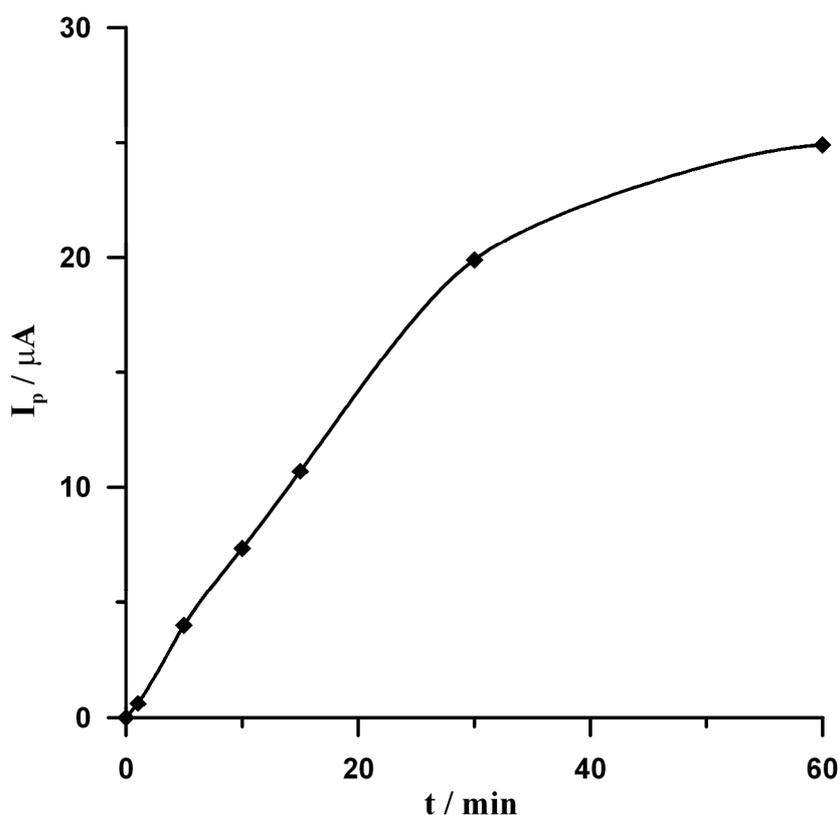


Fig. 3: Effect of the accumulation time on the peak current of Hg(II) at concentration of $1 \times 10^{-6} \text{ mol L}^{-1}$. Experimental conditions: amount of MPTMS in the starting sol: 10%, content of lead powder in sol: 10 g L^{-1} ; SWASV: electrolysis potential: -0.7 V vs. ref., electrolysis time: 60 s, frequency: 25 Hz, step height: 4 mV, and amplitude: 25 mV (other conditions as in Fig. 1).

Factors Affecting the Detection Process

Electrolysis Potential. The anodic peak currents of mercury were evaluated as a function of the electrolysis potential between -0.8 to -0.4 V . For this purpose preconcentration of Hg(II) at concentration of $1 \times 10^{-6} \text{ mol L}^{-1}$ was carried out under stirring for 60 s. The accumulated

species of Hg(II) were desorbed and reduced at -0.7 V for 60 s. It was observed that the anodic peak currents were nearly stable as the potential was changed from -0.75 to -0.6 V and then significantly decreased. Thus -0.7 V was chosen as the electrolysis potential in further studies.

Electrolysis Time. As the detection step implies desorption of Hg(II) species previously accumulated in the preconcentration solution and their subsequent electrolysis (reduction to metallic mercury) prior to their anodic stripping analysis, the quantitative character of measurements is expected to be affected by the effectiveness of these two processes. The complete desorption and reduction can be achieved by appropriate selection of detection medium and by applying an electrolysis time long enough to ensure the quantitative reduction of all Hg(II) species. The detection solution (3 mol L^{-1} HCl) was used in all experiments, according to the data described in literature [13,14]. The effect of electrolysis time on the voltammetric response was studied for the accumulation time of 60 s and Hg(II) concentration of $1 \times 10^{-6} \text{ mol L}^{-1}$. It was observed that the peak current increased as the electrolysis time was increased from 0 to 120 s and remained constant from 120 to 240 s. Therefore, a 120 s electrolysis period was chosen for further study.

Calibration Graph and Limit of Detection

The calibration graph for the accumulation time of 60 s was linear from 5×10^{-8} to $1 \times 10^{-5} \text{ mol L}^{-1}$ and obeyed the equation $y = 0.609x - 0.0152$, where y and x are the peak current (μA) and folic acid concentration ($\mu\text{mol L}^{-1}$), respectively. The correlation coefficient (r^2) was 0.997. The relative standard deviations for a mercury concentration of $1 \times 10^{-6} \text{ mol L}^{-1}$ were 3.9 % ($n = 5$) and 4.7 % ($n = 20$). The detection limit for an accumulation time of 60 s estimated from 3 times the standard deviation for the lowest determined concentration of Hg(II) was about $1.9 \times 10^{-8} \text{ mol L}^{-1}$. It has to be noted, that the detection limit can easily be improved by the prolongation of the accumulation time up to 30 min. The favourable performance of the lead powder-modified thiol-functionalized polysiloxane film electrode is supported by the detection limit value, significantly lower than those found for other sensors based on organically modified mesoporous silica for the accumulation time of 60 s [11-14]. The anodic stripping voltammograms obtained in the course of the determination of increasing concentrations of Hg(II) at the lead powder-modified thiol-functionalized polysiloxane film electrode are presented in Fig 4.

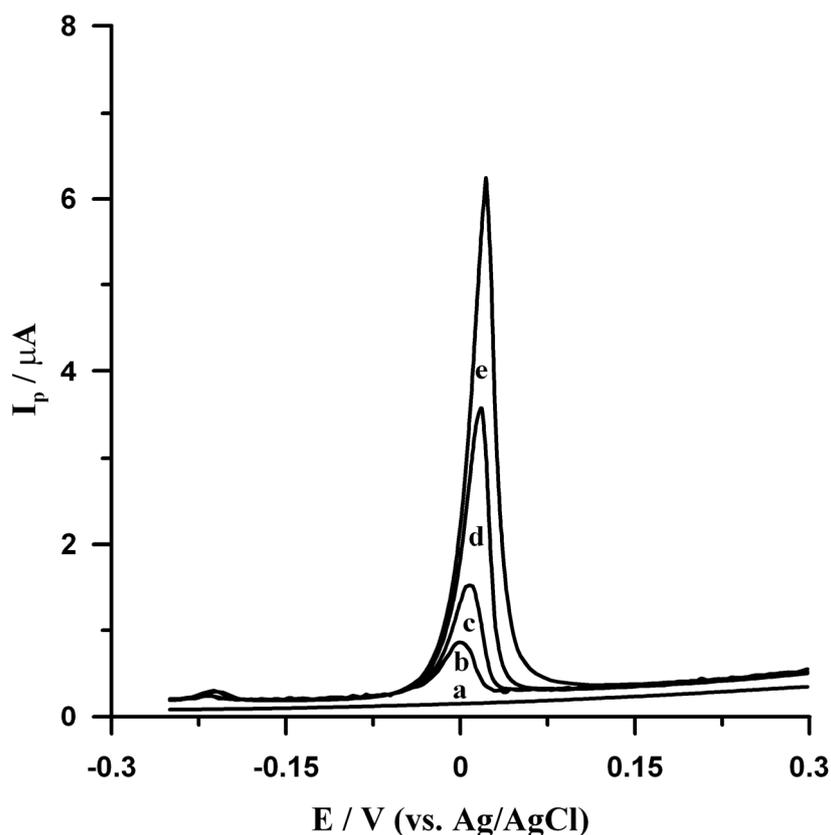


Fig. 4: Square wave anodic stripping voltammograms obtained in the course of the determination of increasing concentration of Hg(II) at the lead powder-modified thiol-functionalized polysiloxane film electrode. Legend: a) blank, b) as (a) + 1×10^{-6} mol L⁻¹ Hg(II), c) as (a) + 2×10^{-6} mol L⁻¹ Hg(II), d) as (a) + 5×10^{-6} mol L⁻¹ Hg(II), e) as (a) + 1×10^{-5} mol L⁻¹ Hg(II). Experimental conditions: amount of MPTMS in the starting sol: 10 %, content of lead powder in sol: 10 g L⁻¹; SWASV: accumulation time: 60 s, electrolysis potential: -0.7 V vs. ref., electrolysis time: 120 s, frequency: 25 Hz, step height: 4 mV, and amplitude: 25 mV (other conditions as in Fig. 1).

Conclusions

In this paper, the preparation and application lead powder-modified thiol-functionalized polysiloxane film electrode is described for the first time. This novel type of lead-based electrodes was prepared by mixing of lead powder with functionalized polysiloxane sol. The investigated electrode was tested as sensors for the anodic stripping voltammetric determination of mercury traces in solution of 3 mol L⁻¹ hydrochloric acid. This report is an initial study and requires further more detailed investigations (e.g., interference study, advanced optimization of key experimental parameters, study of the surface morphology, validation using certified reference materials and application to real samples). However, it

was showed that the lead powder-modified thiol-functionalized polysiloxane film electrode provides a much better electrochemical performance compared to a bare glassy carbon electrode and unmodified thiol-functionalized polysiloxane film electrode. The obtained results show that the investigated electrode is an interesting device for the determination of Hg(II).

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