Phosphonic acid derivative-CME and Coenzyme A-CME for the detection of Uranium (VI)

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The preparation and characterization of two chemically modified gold electrodes (CMEs) for the detection of Uranyl cation have been described. The described CMEs were obtained by chemisorption of a thiolated ethyl ester of phosphono-pentanoic acid and on Coenzyme A. The latter compound is commercially available, while the first was synthetized in our laboratories. Both CMEs have been characterized by electrochemical techniques and employed in Anodic Stripping Voltammetry. Both phosphonic acid derivative and Coenzyme A appeared to be effectively involved in the formation of a complex with the Uranyl ion but, unfortunately, these CMEs displayed insufficient stability at the working conditions necessary for the determination. In order to by-pass this problem, these CMEs could be employed in the preconcentration step only. Further investigations in this direction are currently on progress.

1 Introduction

Uranium and its salts are both radiologically and chemically toxic, as they can cause kidney damage and acute arterial lesions [1]. Concentrations of uranium compounds in natural and contaminated groundwater are typically at very low levels, increasing the difficulty of accurate analysis.

Adsorptive stripping voltammetric techniques have been shown to be able to overtake these problems, as uranium chelates can be preconcentrate on electrode surface prior to the detection step. Sensors based on voltammetric techniques are also well suited for on-site characterization of uranium [2, 3].

These approaches employ mercury drop electrodes [2–11] or iridium-based mercury [12] electrodes; these electrodes are mechanically unstable and toxic mercury, at the end of the analysis, has to be disposed, thus they are less desirable than solid-state sensors in routine field applications [2, 12].

Solid-state carbon paste electrodes modified with ligands for uranium detection have been reported previously [2]. However, the ligands are not strongly bound to the electrode surface, and bleeding of the complexant is observed during the analytical step. Yantasee et al. described an electrode modified with carbamoylphosphonic acid [13], immobilized via covalent bonding onto a high surface area mesoporous silica substrate. The ligand-bearing mesoporous silica was then embedded in a carbon graphite matrix. This CME proved to be selective for actinide ions.

To avoid disadvantages associated with the employment of CPE, we considered the possibility to bind the ligand to a gold surface, thus obtaining a stable and organized monolayer.

We planned to design a thiolic derivative, bringing a phosphonic group. The most suitable phosphonic derivative was 5-mercapto-2-phosphono-pentanoic acid ethyl ester (Figure 1a), chosen owing to its accessible synthesis. This compound can be obtained as ethyl ester [14]. The acidic derivative is obtained through an in situ hydrolysis of the ester, previously assembled on the gold surface.

The response towards Uranyl was also tested for Coenzyme A, as it brings phosphate moiety, omega-thiol functionality and is commercially available (Figure 1b).
2 CMEs preparation and characterization

2.1 Materials and methods

Electrochemical experiments were carried out with Amel 433/W polarographic analyser equipped with a standard three-electrode cell with a gold electrode as working electrode (2.0 mm diameter), a platinum wire as auxiliary electrode and an Ag/AgCl/KCl (4M KCl saturated with AgCl) reference electrode. Reagents were of the purest grade available purchased from Fluka, Acros Organics or Sigma-Aldrich and used as received. Uranium diluted solutions were daily prepared in ultrapure grade water (Milli-Q, Millipore) from a standard 1000 mg/L solution, obtained by weighing the appropriate amount of Uranyl Acetate (Fluka, ACS grade) and dissolved in Milli-Q water. This solution was stable for at least 1 month and was used daily to prepare standard solutions of 100 and 10 mg/L U(VI). All glassware was carefully cleaned with concentrated nitric acid and Milli-Q water to avoid contamination.

2.2 Synthesis of 2-(diethoxy-phosphoryl)-5-mercapto-pentanoic acid ethyl ester and in situ hydrolysis

The phosphonic acid derivative was synthetized as 2-(diethoxy-phosphoryl)-5-mercapto-pentanoic acid ethyl ester (III), and then it was employed for SAM preparation and finally in situ hydrolysed to give the CME of interest (Figure 1(V)). The ester III was synthesized according to the procedure reported by Korte and Wiese [14]. Intermediate products were characterized by $^1$H-NMR.

2.2.1 2-(Diethoxy-phosphoryl)-pent-4-enoic acid ethyl ester (II)

A mixture of (diethoxyl-phosphoryl)-acetic acid ethyl ester (I) (22.4 g, 100 mmol) and allylbromide (16.8 g, 140 mmol) was heated to 60°C. A solution of sodium ethylate (120 mmol, prepared from 2.75 g Na) in absolute ethanol (50 mL) was then added dropwise. Afterwards, the mixture is heated to reflux (1 h), then ethanol is removed under vacuum. The obtained product is dissolved in diethyl ether, and solid NaBr is removed. Ether is finally removed under vacuum, obtaining the product as an oil, which is distilled to give the desired product (22.3 g, 850 mmol, 85% yield).
2.2.2 5-Acetylsulfanyl-2-(diethoxy-phosphoryl)-pentanoic acid ethyl ester (III)

To freshly distilled \( II \) (22.3 g, 850 mmol), dibenzoylperoxide (50 mg, 0.2 mmol) is added at room temperature. Thioacetic acid (7.6 g, 100 mmol, previously distilled) is then immediately added. After about 5 minutes temperature spontaneously reaches 120\(^\circ\)C. If reaction does not start spontaneously, the mixture can be briefly heated at 40-50\(^\circ\)C. The mixture is stirred for 14 hours, then thioacetic acid is removed by distillation at 90\(^\circ\)C. Further distillation provides the desired product, as a colourless oil (24.9 g, 731 mmol, 86% yield).

2.2.3 Preparation of phosphonic derivative-CME and CoA-CME

The gold disk cross section exposed (diameter 2.0 mm) was abraded with successively finer grades of alumina (from 1 \( \mu \)m to 0.05 \( \mu \)m) and then rinsed with water and briefly cleaned in an ultrasonic bath to remove trace alumina from the surface.

SAMs were prepared by dipping the cleaned gold electrode in 5 mM ethanolic solution of phosphonate derivative III or of CoA for 12 hours. To prepare the phosphonic derivative CME, after this step the electrode is rinsed with ethanol and DCM and submitted to \textit{in situ} hydrolysis.

2.3 Electrode characterization

Bare gold electrode double layer capacitance was 75 \( \pm \) 3 \( \mu \)F/cm\(^2\), while Phosphonic Acid derivative SAM and CoA SAM capacitance were 45 \( \pm \) 2 \( \mu \)F/cm\(^2\) and 39 \( \pm \) 1 \( \mu \)F/cm\(^2\) respectively (mean values and standard deviations are calculated from three independent measurements on the same electrode).

The adsorption trends for phosphonic acid derivative and CoA were evaluated following the variation of capacitance with time. The trends obtained are represented by Langmuir model.

The coverage degree was evaluated through reductive desorption in alkaline solution (0.5M KOH, CV, \( E_i \) 200 mV, \( E_f \) -1400 mV, scan rate: 100 mV/s): \( \Gamma \) (CoA) = 3.8 \( \cdot \) 10\(^{-9}\) (mol/cm\(^2\)), \( \Gamma \) (Ph. Acid derivative) = 3.4 \( \cdot \) 10\(^{-9}\) (mol/cm\(^2\)).

3 CMEs response towards Uranyl: results and discussion

3.1 Open circuit preconcentration

Both phosphonic acid and CoA CMEs demonstrated to be effective for detecting U(VI) in aqueous solution using adsorptive stripping voltammetry (AsSV). The process of U(VI) detection involves several steps.

U(VI) in 0.1 M KCl (pH 4) was first accumulated on the electrode surface during an open circuit preconcentration step. The electrode is then removed, abundantly rinsed with water and placed into the polarographic cell for the following electrochemical steps.

Desorption of the preconcentrated uranium ions from the complex is performed in 0.1 M KCl/HNO\(_3\) at pH 2. Concurrent with the desorption process, cathodic electrolysis is performed to reduce U(VI) to insoluble, lower oxidation-state uranium species (\( E_{dep} \) = -800 mV; \( t_{dep} \) = 60 s). The detection step, by anodic stripping voltammetry, is performed in the same acidic solution (\( E_i \) = -800 mV; \( E_f \) = +200 mV).

3.2 Results

A signal related to U(VI) was effectively obtained: uranyl is therefore accumulated on the electrode surface during the open circuit preconcentration step. A signal of 230 nA at -303 mV was obtained for 5 mg/L of U(VI) and 20 minutes of preconcentration. As the signal was lost after a few scans, different buffers and pH were tested, but no advantages were gained. Similar results were obtained with CoA.

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3.3 Desorptive degradation of the monolayer

A possible explanation for these results could be the occurrence of some degradation of the SAM, at the working conditions during the electrochemical step. At sufficiently negative potentials, alkanethiol monolayers are reductively desorbed from the surface to an alkanethiolate which is associated with, but not chemisorbed to, the electrode [15]. The origin of the destruction of the monolayer could also be caused by hydrogen evolution occurring at negative potential, especially at low pH [16].

The potential applied in the cathodic electrolysis step (-800 mV vs. Ag/AgCl) is negative enough for a consistent damage by reductive desorption. In order to verify this hypothesis, the presence of the SAM after the applied working conditions was checked by a classical procedure of reductive desorption in KOH. The result of these investigations showed indeed an evident depletion of the SAM after few scans. Figure 12 shows the comparison between the electrode coverage, by means of reductive desorption, before (a) and after use (b) in the applied working conditions. No signal at all could be obtained if the deposition potential was not al least of -800 mV, condition necessary for the SAM stability.

4 Conclusions

Both phosphonic acid derivative and Coenzyme A appeared to be effectively involved in the formation of a complex with the Uranyl ion but, unfortunately, these CMEs displayed insufficient stability at the working conditions necessary for the determination.

In order to by-pass this problem, we could employ the phosphonic derivative SAM in the preconcentration step only, and employ a second electrode for the electrochemical reduction and stripping steps. Experiments in this direction are currently on progress.

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References