



A ω -mercaptoundecylphosphonic acid chemically modified gold electrode for uranium determination in waters in presence of organic matter



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ABSTRACT

A chemically modified electrode (CME) on a gold surface assembled with a ω -phosphonic acid terminated thiol was investigated for its capability to complex uranyl ions. The electrode, characterized by electrochemical techniques, demonstrated to be effective for the determination of uranyl at sub- $\mu\text{g L}^{-1}$ level by differential pulse adsorptive stripping voltammetry (DPAdSV) in environmental waters, also in presence of humic matter and other potential chelating agents. The accuracy of the measurements was investigated employing as model probes ligands of different complexing capability (humic acids and EDTA).

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1. Introduction

Uranium commonly exists in the environment in the U(VI) and U(IV) oxidation states, and the most stable chemical species in aqueous solution under oxic conditions is the uranyl ion (UO_2^{2+}) [1]. Concentrations of uranium in contaminated groundwater are typically very low ($0.03\text{--}2.1 \mu\text{g L}^{-1}$ in surface waters and $0.003\text{--}2.0 \mu\text{g L}^{-1}$ in ground waters) [2] but, due to its toxicity [3], accurate analyses are mandatory even at these low concentrations. As concerning drinking water, there is up to now no binding statutory maximum levels for uranium either in Europe or in Western Countries. This also applies to mineral, spring and table water, although it is recommended that drinkable waters for infant use should not contain more than $2 \mu\text{g L}^{-1}$ total uranium. This assessment is based on the International Guidelines for Drinking Water Quality of the World Health Organization (WHO), that also suggested a guideline value for uranium of $30 \mu\text{g L}^{-1}$ for waters intended for human consumption [4]. Hence, individual countries can establish own guideline values; as an example, in Germany, the Federal Environmental Agency (UBA), responsible for assessing drinking water quality, recommends compliance with a slightly more restrictive guideline value of $10 \mu\text{g L}^{-1}$ water [5].

In view of this premise, several methods for the determination

of trace amounts of uranium in various water samples have been developed. Common analytical techniques involved ICP-MS, in some cases combined with ion chromatography [6] and radio-metric techniques [6,7]. Moreover, neutron activation analysis [8] and electrochemical methods, such as adsorptive stripping voltammetry [9–11] have been also proposed. Electroanalytical methods usually have the advantage of instrumental simplicity and relatively low cost. Sensitive voltammetric techniques using mercury electrodes [12], or Hg film on iridium and carbon covered with lead have been proposed [13], although with some concern from the environmental point of view. More environmental-friendly approaches were developed, based on adsorptive stripping voltammetry at solid electrodes. These potentially portable devices are lightweight, compact, and readily automated [14]; LOD are in the nanomolar range, using quiet long deposition times (> 13 min, LOD $1.35 \mu\text{g L}^{-1}$ [15]; > 20 min, LOD $1 \mu\text{g L}^{-1}$ [16]).

Recently, sensitive detection of uranyl has been carried out at bare vibrating gold electrodes using square wave voltammetry (LOD $0.24 \mu\text{g L}^{-1}$, 300 s deposition time [17]) or on graphite screen printed electrodes [18]. However, the use of solid electrodes is often precluded due to memory effects, passivation of the surface and high background currents, and thus the use of modified electrodes is in this way encouraged. Indeed, chemical derivatization of the electrode surface (to obtain a chemically modified electrode, CME) can lead to increased electrocatalytic activity, selectivity and sensitivity. Common modification strategies employ self-assembled monolayers (SAMs) electrodes, in particular SAMs

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on gold surfaces, which allow manipulation in molecular scale to obtain highly ordered and stable recognition systems [19–21]. These last can be prepared from thiols, disulphides, and sulphides, and are chemically resistant over a wide range of temperature, pH, and electrical potential. Moreover, selectivity toward specific analytes can be obtained by tuning the chemical nature of the monolayer [20,22]. Despite these attractive premises, there are only few reports about uranium determination at CMEs in the most recent literature. A ω -phosphate terminate SAM on gold with LOQ of about $250 \mu\text{g L}^{-1}$ (as uranyl) with 20 min deposition time was presented by Becker et al. [23]; better results were obtained on a self-assembled ensembles of a disulphide derivative of calixarene on polycrystalline gold (LOQ of $10 \mu\text{g L}^{-1}$ as UO_2^{2+}) [24] and on a graphite electrode chemically modified with a palmitoyl- α -ascorbic acid, with LOD of $0.26 \mu\text{g L}^{-1}$ with 30 min pre-concentration time [25]. Starting from the consideration that phosphonate is a strong ligand for metal ions [23] and that ω -derivatized phosphonic acid terminated thiols are now commercially available (Sigma-Aldrich), we were encouraged to use 11-mercaptoundecylphosphonic acid (MUPA) to form a SAM on a gold electrode, exploiting its ability to bind uranyl, due to the high complexation constant of the parent phosphonic acids for this ion and the relative selectivity of the interaction [26].

We report herein a differential pulse adsorptive stripping voltammetry (DPAdSV) method for the quantitative determination of uranyl in waters at a gold surface electrode modified with a ω -alkanephosphonic acid terminated thiol. The method was applied to the analysis of waters at different salinity, obtaining LOD of $0.1 \mu\text{g L}^{-1}$ with 1000 s preconcentration time. The influence of ligands that can be found in natural waters was investigated using humic acids and EDTA as probes of different complexing capability.

2. Experimental section

2.1. Materials and reagents

Reagents of the purest grade available were purchased from Sigma-Aldrich and used as received. All the solutions were prepared by Milli-Q water. Uranyl standard (Aldrich, standard for ICP-OES, 1000 mg L^{-1}) was used daily to prepare daily diluted standard solutions.

11-mercaptoundecylphosphonic acid, $\text{K}_3\text{Fe}(\text{CN})_6$ and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ were obtained from Sigma-Aldrich. All glassware was carefully cleaned with concentrated nitric acid and then rinsed with Milli-Q water in order to avoid contamination.

Electrochemical measurements were carried out with BASI PWR-3 power module and EF-1085 C-3 cell stand, equipped with a gold electrode (geometrical area 0.020 cm^2), modified as below described, as working electrode; an Ag/AgCl/NaCl (3 M NaCl, saturated with AgCl) reference electrode and a platinum wire as auxiliary electrode, both obtained from BASI.

KCl buffer solution (0.1 M in Milli-Q water) was conserved over Chelex (1 g/100 mL) and diluted with Milli-Q water prior to use.

Throughout the paper, the standard deviation between parentheses refers to the uncertainty of the last digit. Mean values, unless otherwise specified, are calculated for $n=3$. All measurements and constants reported in the manuscript refer to 25 °C.

2.2. Gold electrode pre-treatment

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

Abrasion favours oxidation of gold surface (as can be noticed by cyclic voltammetry), so it was necessary to perform an electrochemical cleaning before the SAM preparation, by cycling the potential between 0.0 V and +1.40 V in 0.5 M H_2SO_4 solution, with a scan rate of 200 mV s^{-1} , until Au oxidation and reduction peak currents reach a constant value (20 cycles are usually enough).

2.3. Electrode modification

The CME was modified by dipping the bare gold electrode overnight in a solution containing 2.5 mM MUPA and 2.5 mM tributylphosphine in methanol. The modified electrode was then abundantly rinsed with ethanol and Milli-Q water before use.

2.4. Electrodes characterization

Before modification, bare gold electrode area was estimated electrochemically by cyclic voltammetry (CV) [27], using 1 mM ferrocene (in acetonitrile containing 0.1 M tetrabutylammonium perchlorate); an Ag/AgCl/3 M NaCl reference electrode (BASi) was used. The anodic and cathodic peak currents of the ferrocene redox couple were plotted as a function of the square root of the scan rate (in the range $10\text{--}500 \text{ mV s}^{-1}$). The electrode area was calculated according to the modified form of the Randles-Sevcik equation:

$$I_p = (2 \cdot 69 \cdot 10^5) n^{3/2} A D^{1/2} C_\infty \nu^{1/2} \quad (1)$$

where: C_∞ is the concentration of ferrocene in the bulk solution (mol cm^{-3}), n is the electron stoichiometry ($n=1$), I_p is peak current (Ampere), A is electrode area (cm^2), D is diffusion coefficient ($2 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at $T=298 \text{ K}$) and ν is the scan rate (V s^{-1}).

The SAM electrode was characterized with usual electrochemical techniques, and following a general, well-known and widely used approach [28]. In detail, the presence of the monolayer was checked by measuring the double layer capacitance of the electrode before and after SAM formation; this parameter is related to the effective thickness, the dielectric constant, and the order degree of the SAM [27,29], as it strongly depends on the presence of functional groups able to influence the dielectric constant of the monolayer [30]. The working conditions applied were: potential scan from 0 mV to +300 mV, in 0.1 M KCl, at different scan rates (typically from 10 mV s^{-1} to 200 mV s^{-1}); the differences between the anodic and cathodic charging currents, measured at 150 mV, were plotted vs. the scan rates, and the double layer capacitance is obtained from the slope of the linear regression, divided by twice the electrode area [27]; this approach produces results virtually unaffected by faradaic contributions.

The variation of the capacitance for different immersion times in the MUPA solution was used to follow the adsorption kinetics of the thiol onto the gold substrate [31], while the measurement of interfacial capacitance provides a convenient way for evaluating the degree of surface coverage, θ , of the organic adsorbates. It can be obtained using the expression [32, 33]:

$$\theta = (C_0 - C_t)/(C_0 - C_f) \quad (2)$$

where C_0 is the bare electrode capacitance, C_t is the capacitance at any time t , and C_f is the capacitance of the fully covered monolayer. The variation of the degree of surface coverage, $\theta(t)$ with time t is expressed by the following relation:

$$\theta(t) = [1 - \exp(-kt)] \quad (3)$$

where k is the adsorption rate constant.

Surface coverage (Γ , mol cm^{-2}) can be estimated by reductive desorption of thiol from the electrode surface. The film desorbs in alkaline ($\text{pH} > 11$) solution through the reductive path in reaction

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