



An electrochemical sensor for trace uranium determination based on 6-O-palmitoyl-L-ascorbic acid-modified graphite electrodes

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ABSTRACT

The development of a preconcentrating sensor based on 6-O-palmitoyl-L-ascorbic acid (PAA)-modified graphite (GRA) electrodes for the determination of uranium is described. PAA, a water insoluble compound of ascorbic acid, was immobilized onto the surface of the GRA electrodes through physical adsorption from acetone solutions. Uranium was accumulated by heterogeneous complexation (10 min, in 0.1 M H₃BO₃, pH 4.3) and then, it was reduced by means of a differential pulse voltammetric scan in 0.1 M H₃BO₃, pH 3.4. Alternatively, the performance of both preconcentration and voltammetric steps in a single run, at 0.1 M H₃BO₃, pH 3.65, was also examined; however, in this case the observed current signals were lower by 30%. The experimental variables were investigated and under the selected conditions, a linear calibration curve in the range 2.7–67.5 μg L⁻¹ U(VI) was constructed ($r^2 = 0.9981$). The 3σ limit of detection and the relative standard deviation of the method were 1.8 μg L⁻¹ U(VI) and 8% ($n = 5$, 20 μg L⁻¹ U(VI), preconcentration time 10 min), respectively. By increasing the preconcentration time to 30 min, a limit of detection as low as 0.26 μg L⁻¹ U(VI) can be achieved. The effect of potential interferences was also examined. The accuracy of the method was established by recovery studies in inoculated tap and lake water samples. A simple and fast procedure based on filtering of the sample through a C-18 microcolumn was successfully used to remove the organic matter from the lake water samples.

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1. Introduction

Uranium is a toxic element that occurs naturally in most rocks in concentrations of 2–4 μg kg⁻¹, and, in much lower concentrations, in surface (0.03–2.1 μg L⁻¹) and ground (0.003–2.0 μg L⁻¹) water. In seawater the concentration is about 3.0 μg L⁻¹ [1]. Uranium, can, also, enter the environment as a consequence of several technological processes, such as burning of fossil fuels, nuclear weapons fabrication and testing, nuclear fuel cycle processes, radioisotopes production and application and nuclear accidents. Due to the uranium intake in human body, especially from water, vegetables, cereals and table salt, its monitoring in the environment is essential [2].

Radiometric techniques (alpha-, gamma spectrometry and liquid scintillation counting) [3], inductively coupled plasma-mass spectrometry (ICP-MS) [4] and neutron activation analysis [5] can be successfully used for the determination of uranium; however, these methods are not cost-effective and are, mostly, available in centralized laboratories. On the other hand, electroanalytical techniques are simpler in means of equipment and expenditure and yet

are potent tools for the determination of uranium in water samples. Among them, various procedures based on solution-phase voltammetry on mercury electrodes have been proposed [6,7]. However, sensitivity issues do not allow their application to the direct monitoring of uranium in environmental samples. Contrary to these methods, adsorptive stripping voltammetry (AdSV), which relies on complexation of uranium with a surface-active ligand and adsorptive preconcentration of the complex on the surface of the working electrode, offers low limits of detection and so far it has been extensively used for the determination of uranium in environmental samples. Reagents that have been proposed for the complexation of U(VI) ions, among others, include oxine [8], hydroxyethylpiperazine ethane sulfonic acid [9], cupferron [10], propyl gallate [11], chloranilic acid [12], catechol [13], potassium hydrogen phthalate [14], aluminon [15], 8-hydroxyquinoline [16], pyromellitic acid [17], arsenazo (III) [18] and humic acid [19]. However, mercury, onto which all the above uranyl complexes are absorbed, is not recommended because of its toxicity, and thus, a new type of electrodes, based on less toxic bismuth [20] has been alternatively proposed for the determination of uranium [21,22]. In general, the performance of these electrodes is good, although reported values for both limit of detection and preconcentration time are higher compared with those have been reported at mercury electrodes. Other electrode materials based on lead-coated

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glassy carbon electrodes [23], mercury film silver-based electrodes [24] and iridium-based mercury electrodes [25] have also been proposed; however, in these approaches as well, issues related to environmental considerations are still unsolved.

Despite the excellent in some cases figures of merit of the above electroanalytical techniques, the development of solid-state sensors is also in parallel progress, as, in principle, the latter hold promise for routine, on-site environmental monitoring of uranium. A number of sensors based on solid-state electrodes modified with propyl gallate [26], N-phenylcinnamohydroxamic acid [27], carbamoylphosphonic acid [28], self-assembled monolayers of thiols functionalized with phosphate groups [29,30], nafion [31], calixarenes [32,33], carbon nanotubes [34], and electrochemically produced 4-carboxyphenyl moieties onto graphite electrodes [35] has been proposed the last two decades. In general, the uranyl sensors proposed so far are inferior, in terms of sensitivity and rapidity, compared with the AdSV-based methods. Limits of detection near nM level are usually achievable at prolonged incubation times (>13 min [34,35]; >20 min [28]), whereas, in some cases, the reported limit of detection values are higher than 10 ppb [33], or even, 100 ppb [26,29]. In addition, multistage sensor fabrication or special electrochemical pre-treatment employed in some of the reported methods [29,30,32,35] are not really compatible with cost effective, mass production techniques of sensor fabrication.

In this work, we have explored the possibility of determining uranium in inoculated tap and lake water samples by using a pre-concentrating sensor based on PAA-modified GRA electrodes. The proposed sensors exhibit a high selectivity towards U(VI) ions and the way of their fabrication is compatible with mass production techniques. Application to real matrices, rich in organic matter, was successfully tested by passing the sample through a C-18 microcolumn. Following this simple and fast procedure, the total time of analysis was shortened from several hours (following a common UV-digestion based treatment) to less than 30 min.

2. Experimental

2.1. Chemicals

6-O-palmitoyl-L-ascorbic (PAA) was purchased by Fluka and used as received. All other chemicals used were of analytical grade. Double distilled water (DDW) and polypropylene vessels were used throughout. Vessels were kept in 5% HNO₃ solution and before use, they were extensively washed with DDW. Stock solution of uranyl acetate [5 mM; 0.0212 g of uranium acetate dehydrate (Merck) in 10.0 mL of 0.01 M HCl] was weekly prepared. Working solutions of uranium and other metals were prepared from the above stock solution and 1000 mg L⁻¹ atomic absorption standard solutions, respectively after appropriate dilution with DDW. Solutions of 0.1 M boric acid were prepared by dissolving 3.0915 g of boric acid (Riedel-deHaën) in 1.0 L DDW and pH adjustment to desired values was made with 0.1 M HCl.

2.2. Apparatus

Differential pulse voltammetry (DPV) experiments were conducted with the electrochemical analyzer PGSTAT12 (Metrohm Autolab) in a one-compartment three-electrode cell. Spectroscopic graphite rods (RW0001, 6.5-mm diameter, Ringsdorf-Werke) and a platinum wire were served as the working and auxiliary electrodes, respectively. The reference electrode was a Ag/AgCl/3 M KCl (IJ Cambria) electrode and all potentials reported hereafter refer to the potential of this electrode.

2.3. Preparation of the modified electrodes

Graphite rods were polished on ultrafine emery paper (1200-grit, Struers), then polished against a lens cleaning tissue (No. 105 Whatman), and finally thoroughly washed with DDW. Rods were dried at 60 °C for 30 min, heated in a muffle furnace at 600 °C for 90 s (to remove any particles from the surface), and allowed to cool in a desiccator. To avoid electrical contact between the sides of the electrodes and the solution, the sides of the working electrodes were covered with Parafilm before use.

The surface modification was made by applying 10 μ L of 2 mM PAA solution in acetone on the surface of the electrode with a micropipette. The solvent was allowed to evaporate at ambient temperature for at least 2 h, following thorough washing with DDW. GRA/PAA electrodes were stored in a well-stopped chamber under argon to avoid oxidation of ascorbic acid by oxygen in atmosphere.

2.4. Preparation of the samples

Tap and lake (Lake Pamvotis, Ioannina) water samples were inoculated with different concentrations of U(VI), mixed well and stored in polypropylene bottles at room temperature. Tap water inoculated samples were used without any treatment, while lake water inoculated samples were acidified (25 μ L conc. HCl in 20 mL sample) and passed through a C-18 microcolumn (sep-Pak: Plus tC18, Waters) at a constant flow rate 1 mL min⁻¹ with the aid of peristaltic pump (minipuls3, Gilson). Before use, C-18 microcolumn was conditioned with methanol (2 mL at a flow rate 1 mL min⁻¹) following thorough washing with a dilute solution of HCl.

2.5. Procedure

Adsorptive accumulation of U(VI) onto GRA/PAA sensors was performed for 10 min under mild stirring in a 20.0 mL solution of 0.1 M H₃BO₃, pH 4.3. Then, sensors were rinsed with DDW and transferred to the measuring cell. Reduction of accumulated U(VI) was performed in 0.1 M H₃BO₃, pH 3.4 by applying a DPV scan over the potential range 0.1 to -0.3 V while the voltammogram was recorded. Current intensity of the peak observed at -0.175 V was taken as a measure of U(VI) concentration. Alternatively, both accumulation and voltammetric steps were performed in a single run, in 0.1 M H₃BO₃, pH 3.65.

Recovery studies were made by mixing 16.0 mL of the inoculated tap or lake water samples with 4.0 mL of 0.5 M H₃BO₃, pH 4.3. If necessary, pH was adjusted to 4.3 with 0.1 M HCl, while accumulation and voltammetric steps were carried out as described above.

3. Results and discussion

3.1. Interaction of U(VI) ions with the modified surface

The uranyl ion, a Lewis acid, has a high affinity for hard donor groups. It is highly oxophilic, and addition of it to ascorbic acid results in the formation of a brown complex. Based on spectrophotometric studies, Abdel Razik et al. proposed the formation of a 1:1 complex [36], in accordance with other published works [37]. However, the formation of 1:2 or 1:3 complexes, depending on the concentration of the ligand, has also been reported [38].

The orientation of the immobilized modifier is governed by hydrophobic interactions between the surface of the graphite electrodes and the (hydrophobic) chain of palmitic acid, exposing so the ascorbic acid moieties to the side of the electrolyte. In this regard, the two hydroxyl groups of endiol are easily accessible to various metal ions, among them U(VI), to form complexes. According to the distribution diagrams of uranium in aqueous solutions,

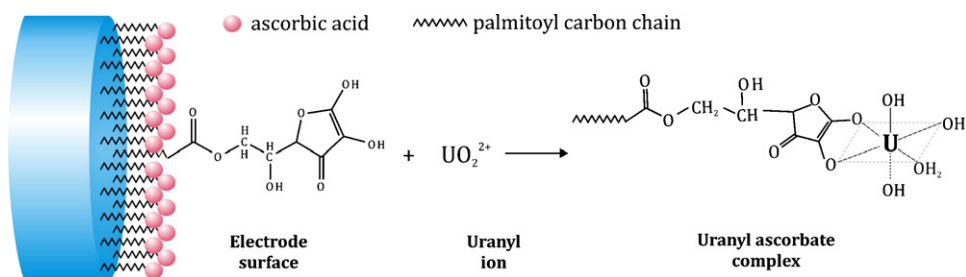


Fig. 1. Tentative view of the interaction of U(VI) ions with the immobilized 6-O-palmitoyl-L-ascorbic.

at pH 4.3 where the preconcentration step was carried out, U(VI) ions exist at UO_2^{2+} and UO_2OH^+ forms at fractions >0.8 and <0.1 , respectively [39]. At this pH, the immobilized molecules of ascorbic acid (as part of the immobilized ester) can be roughly considered as diprotonated, since the hydrogen atoms of endiol are expected to be less acidic compared with those of the free acid ($\text{p}K_{\text{a}1} = 11.6$ and $\text{p}K_{\text{a}2} = 4.1$). On this basis, the formation of an uranyl–ascorbate chelate, as that illustrated in Fig. 1, can be speculated. Uranyl ion is possibly co-ordinated to the hydroxyl groups of the endiol leading, in the presence of two molecules of water, to a four co-ordinate planar bonding arrangement perpendicular to the axial O–U–O unit. The formation of this tetragonal bipyramidal chelate is also proposed by Taqui Khan and Martell in their studies on the catalytic oxidation of ascorbic acid by vanadyl [40] and uranyl [41] ions.

3.2. Selection of the electrode material and electrolyte

At the offset, different electrode materials including gold, platinum, glassy carbon and graphite were examined in their efficiency to probe electrocatalysis of uranium. Comparative cyclic voltammetric experiments in different electrolytes (boric acid, phosphoric acid, acetic acid, formic acid, perchloric acid, nitric acid, sulfuric acid and hydrochloric acid, all at a concentration of 0.1 M) were performed within the pH range 2.5 to 4.5. Adjustment of pH to the desired values was made with 3 M HCl or 3 M NaOH. Best results were observed for gold and graphite electrodes in the presence of boric acid, acetic acid and formic acid. To conclude the most suitable experimental conditions, a series of preliminary DPV experiments, by using PAA-modified gold and graphite electrodes at the three selected electrolytes, at pH 3.5, were further performed. Measurements with GRA/PAA electrodes in boric acid were superior in terms of both sensitivity and background level, and in addition, they showed no influence by the presence/absence of atmospheric oxygen.

The effect of the roughness of the surface on both the sensitivity and the shape of the DPV-grams was also investigated. Graphite electrodes were polished with emery papers of different grids (400, 600, 800, 1000 and 1200) and DPV-grams of the corresponding PAA-modified graphite sensors, in the presence of $13.5 \mu\text{g L}^{-1}$, were compared. Sensitivity was practically constant, while a peak observed at 0.05 V, attributable to the reduction of dehydro-L-ascorbic acid (the oxidized form of ascorbic acid) was effectively removed at graphite electrodes polished with ultrafine emery papers. This peak was more obvious at electrodes with a rough surface, and despite of the electrodes roughness its height was increased during storage of the modified electrodes at open atmosphere.

3.3. Optimization studies

The DP parameters, that is, modulation amplitude, modulation time and interval time were investigated in the range 20–100 mV, 20–60 ms, and 100–200 ms, respectively. The most pronounced

effect on the intensity of the reduction peak of U(VI) at -0.175 V was observed with respect to the modulation amplitude. The uranium peak height increased with increasing values up to 100 mV, and at the same time, the peak potential was shifted to positive direction and the background current increased. The effect of the other DP parameters was examined at a modulation amplitude of 80 mV. The best compromise between sensitivity, background and peak width was achieved with the following conditions: modulation amplitude, 80 mV; modulation time, 30 ms; interval time, 150 ms. Under these conditions the effective scan rate was 40 mV s^{-1} .

The effect of the concentration of the modifier on the performance of the sensor was examined over the concentration range 0.25–4.0 mM PAA. As can be seen in Fig. 2, the response of the sensor with respect to the concentration of PAA in the deposition solution is described by a bell-shaped curve, which exhibits a maximum at 2 mM PAA. At this concentration, an adequate population of properly orientated ascorbic acid moieties has probably been established. At lower concentrations, besides the expected decrease of the number of the binding sites, the orientation of ascorbic acid moieties is probably not suitable, and thus interactions of the target ion with the two hydrogen atoms of endiol become less favorable. As stated above, the orientation of ascorbic acid moieties in the immobilized ester is governed by the hydrophobic interactions among the molecules of the modifier and between them and the surface of the electrode. At a low molar concentration of the modifier, ascorbic acid moieties are expected somehow to lay onto the surface of the electrode. On the other hand, the decrease of the signal observed at higher concentrations of PAA, is probably attributable to steric hindrance of the chelating sites and the concomitant reduced accessibility of the target ions to them.

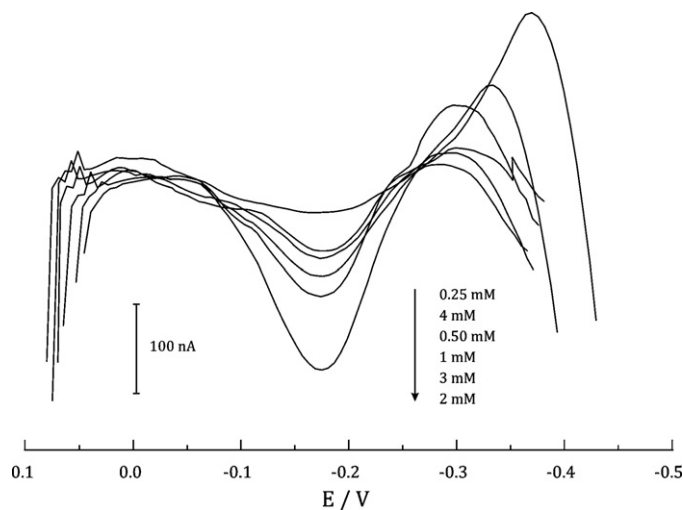


Fig. 2. Effect of the concentration of PAA on the performance of the sensors. $13.5 \mu\text{g L}^{-1}$ of U(VI); Preconcentration step, 0.1 M H_3BO_3 , pH 4.3, 10 min; measurement step, 0.1 M H_3BO_3 , pH 3.4; DPV parameters: modulation amplitude, 80 mV; modulation time, 30 ms; interval time, 150 ms.

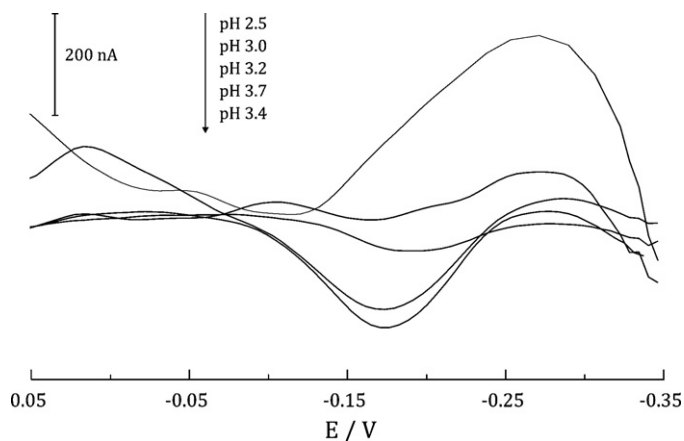


Fig. 3. Effect of the pH of the stripping solution on the voltammetric peak of uranium at the two-step procedure. Conditions as in Fig. 2.

Optimum pH values for each preconcentration and voltammetric step at the two-step procedure, as well as, the optimum pH value for the common preconcentration/voltammetric step at the single run procedure were selected by performing a series of experiments in 0.1 M H_3BO_3 , covering the pH ranges 4–6.5, 2.5–3.7 and 3.2–3.8, respectively. pH profile for the preconcentration step exhibits a maximum at pH 4.3. In accordance with previous studies [42], the formation of the uranyl–ascorbate complex is favored within the pH range 4.2–4.5, and, under these conditions, it exhibits a maximum stability for about 24 h. pH profile for the measuring voltammetric step is quite different compared with that observed in the preliminary cyclic voltammetric studies (see Section 2.2). It is noted however, that, DPV measurements were performed with PAA-modified graphite electrodes, contrary to CV studies that made with bare graphite electrodes. Well-defined peaks were observed only within a narrow pH range between 3.4 and 3.7, and thus a pH value of 3.4 was selected for subsequent experiments. As illustrated in Fig. 3, at more acidic conditions ($\text{pH} < 3$), the shape of the received DPV-grams is seriously altered. Finally, by performing the method in a single run, optimum results were received at pH 3.65.

The effect of the preconcentration time on the response of the sensors was also examined in a solution of 0.1 M H_3BO_3 , pH 4.3 containing $6.75 \mu\text{g L}^{-1}$ U(VI). The response of the sensor was increased

almost linearly upon the preconcentration time up to 60 min indicating that the kinetics of the reaction is rather slow.

3.4. Analytical features of the method

Using a preconcentration time of 10 min, a linear relationship was obtained between the current of the reduction peak at -0.175 V ($I_p/10^{-8} \text{ A}$) and the U(VI) concentration in the range 1×10^{-8} – $2.5 \times 10^{-7} \text{ M}$ (2.7 – $67.5 \mu\text{g L}^{-1}$) with a correlation coefficient, $r^2 = 0.9981$ (Fig. 4). The 3σ limit of detection and the relative standard deviation of the method were $1.8 \mu\text{g L}^{-1}$ U(VI) and 8% ($n=5$, $20 \mu\text{g L}^{-1}$ U(VI)), respectively. At the cost of a longer preconcentration time (30 min), a lower limit of detection of $0.26 \mu\text{g L}^{-1}$ U(VI) was achieved.

3.5. Interference study

The response of the proposed sensors to various ions present in real samples, as well as, to some ions with similar physical or chemical properties with the ion of interest was investigated using standard solutions of each of the tested ions at concentrations $\geq 100 \mu\text{g L}^{-1}$. Corresponding DPV-grams, along with that of U(VI) at a concentration of $2.7 \mu\text{g L}^{-1}$, which used for comparison, are shown in Fig. 5. As(V), Cd(II), Cr(VI), Fe(III), La(III), Mn(II), Pb(II), Sb(V) did not interfere at all, whereas, the observed $I_p(\text{ion})/I_p(\text{U(VI)})$ ratio for Hg(II), Ni(II), Se(IV) and Th(IV) was < 0.15 . In the presence of Cu(II) ions, the sharp peak at $+0.050 \text{ V}$ is identical to that observed when GRA/PAA electrodes left to open atmosphere for a long period of time, and thus it can be attributed to the reduction of dehydroascorbic acid and to cupric ions catalyzed oxidation of ascorbic acid [43]. On the other hand, in the presence of vanadyl ions, the peak observed at -0.050 V is attributable to the formation of a 1:1 complex of vanadyl–ascorbate, similar to that of uranyl–ascorbate [40]. An identical peak was observed during the cathodic DPV scan of graphite electrodes, on which $10 \mu\text{L}$ of a $10 \mu\text{g L}^{-1}$ VO^{2+} solution had been applied and allowed to dry.

The selectivity of the GRA/PAA sensors was further supported by performing measurements at mixed solutions containing $6.75 \mu\text{g L}^{-1}$ U(VI) and a 10-fold mass concentration excess of Fe(III), La(III), Mn(II), Pb(II), Hg(II), and Th(IV). Taking as criterion a $\pm 10\%$ error in the peak heights, none of the above metals interfered.

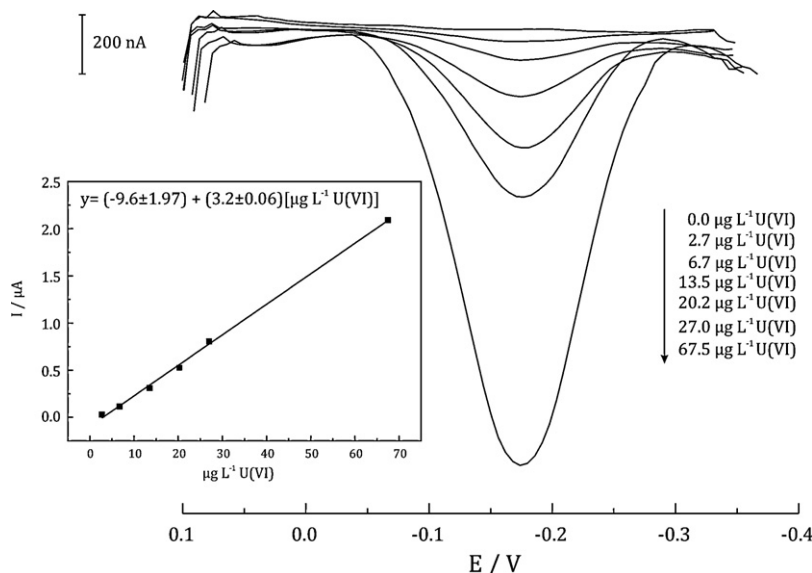


Fig. 4. Response of the GRA/PAA sensors to different concentrations of U(VI). The inset graph illustrates the respective calibration curve. Conditions as in Fig. 2.

Table 1
Recovery studies.

Sample	Added ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)	Remarks
Tap water	2.70	2.76	102.3	
	6.75	7.19	106.5	
	13.50	13.73	101.7	
Lake water	6.75	N.D.	–	
	13.5	1.9	15	
Lake water after treatment with a C-18 microcolumn	2.70	2.84	105.4	Analysis was performed at an acidified sample 1 h after inoculation
	6.75	6.86	101.7	as above
	13.50	13.98	103.6	as above
	13.5	14.7	109.3	Analysis was performed at an acidified sample 1 week after inoculation
	13.5	4.2	31.2	Analysis was performed at a non-acidified sample 1 week after inoculation
	13.5	14.2	105.7	Analysis was performed at an acidified sample 1 month after inoculation
	13.5	4.1	30.4	Analysis was performed at a non-acidified sample 1 month after inoculation

^a Mean value from duplicate measurements.

3.6. Recovery studies

The accuracy of the method and the effect of the matrix of the real samples were assessed by recovery studies adding standard uranyl solutions to tap and lake water samples. As shown in Table 1, recoveries ranged from 102% to 107%, proving so the suitability of the GRA/PAA electrodes for application to real samples. The original content in uranium was checked by applying the method for an accumulation period of 60 min.

Among the various procedures have been proposed for the removal of the organic content from a sample in order to avoid fouling of the surface of the electrode and matrix effects, UV digestion has been successfully used in many electrochemical applications [21]. However, it is a time-consuming procedure (typically takes 4–5 h), thus extending the total time of analysis. Here, we explored an alternative procedure, which based on the passing of the acidified sample through a hydrophobic C-18 microcolumn. Using a typical flow rate of 1 mL min^{-1} , the time required for each sample is restricted to a few minutes thereby reducing considerably the overall time of analysis. The recovery values tabulated in Table 1 as well

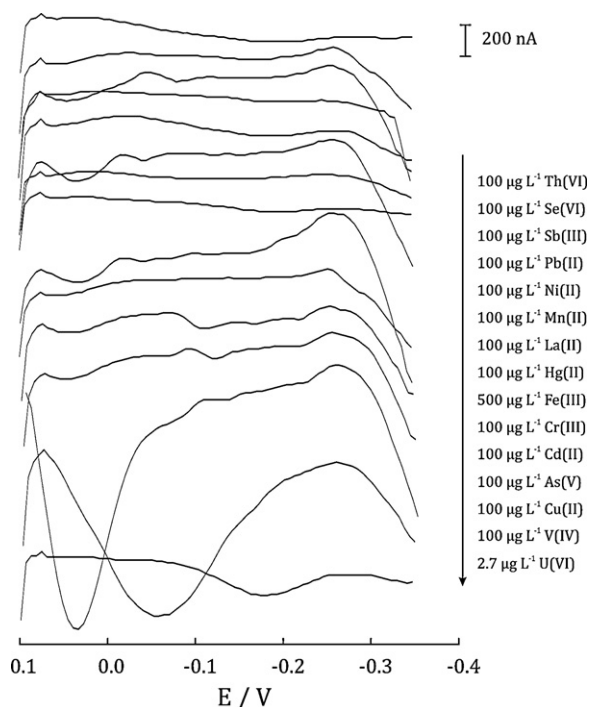


Fig. 5. Response of GRA/PAA sensors to various ions. Conditions as in Fig. 2.

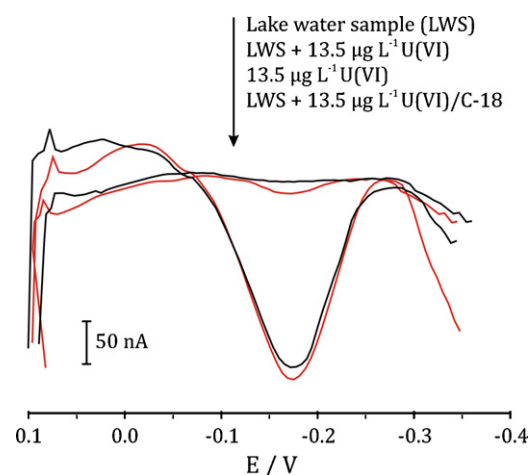


Fig. 6. Recovery of uranium at a lake water sample and at an acidified lake water sample treated in a C-18 microcolumn. Conditions as in Fig. 2.

as the DPV-grams illustrated in Fig. 6, constitute evidence for the effectiveness of the proposed procedure to adequately remove the organic content from the tested sample. However, the widespread usage of the proposed treatment requires first extended studies to be performed in a larger number of samples of different origin. A critical issue is the quantitative release of the bound ions from the matrix. In this regard, acidification of the sample is essential (Table 1). At low pH values, the various metal-binding groups (hydroxyl, carboxyl) are expected to be protonated and thus metal ions are released to the eluent. However, the binding of metal ions to compounds or macromolecules exist in natural samples, is sometimes a slow process and it takes time to complete. In this work, the effectiveness of the proposed treatment was successfully checked over a period of one month. As shown in Table 1, the proposed treatment was performed at acidified and non-acidified 20 mL portions of an inoculated lake water sample, 1 h, 1 week and 1 month after inoculation with uranium.

4. Conclusions

This work describes functional sensors, based on graphite electrodes modified with a water insoluble compound of ascorbic acid, 6-O-palmitoyl-L-ascorbic acid, for the determination of uranium. The proposed sensors were successfully tested for the determination of uranium in inoculated tap and lake water samples. Application to lake water samples, a sample rich in organic matter, was successfully performed by employing a simple and rapid procedure based on the filtering of the sample through a C-18 microcolumn. The proposed sensors are selective to uranium and,

for a preconcentration time ≥ 10 min, they exhibit an adequate sensitivity for application in water samples. In total, the figures of merit of the GRA/PAA sensors are equal or even better compared with those of other sensors that have been so far proposed in the literature. In addition, the way of their preparation is compatible with mass production techniques of electrode fabrication. The development of PAA-modified screen-printed sensors is currently in progress in our laboratory.

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