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Short communication

An adsorptive stripping voltammetry procedure for ultra-trace determination of U(VI) using double accumulation step on two lead-film working electrodes

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ABSTRACT

We report a very sensitive stripping voltammetric procedure for determination of ultra-trace quantity of U(VI) in water samples. A very low detection limit was achieved owing to the application of a new construction of the voltammetric electrode cell with two built-in working electrodes that differed significantly in their surface area. The procedure was based on the double adsorptive accumulation of the U(VI)-cupferron complex onto two lead film working electrodes. Under optimal conditions the detection limit for accumulation time of 120 s for the big electrode and 120 s for the small electrode was about 3.1×10^{-11} mol L^{-1}, whereas for accumulation time of 480 s for the big electrode and 240 s for the small electrode it was about 1.1×10^{-11} mol L^{-1}. The proposed method was successfully validated using certified reference material seawater NASS-5.

1. Introduction

Uranium in the Earth's surface is generally considered to be relatively immobile but it is often released in nature by the weathering of depleted mine tailings and ore wastes [1]. Depleted uranium is a byproduct of the uranium enrichment process and has been used for decades in medical and industrial applications, radiation shielding, counterbalance weights in aircraft and, more recently, in military armor and ammunition [2]. In view of the fact that uranium has been classified as a toxic element, it is necessary to check the environment for uranium pollution. Although uranium can exist in oxidation states U(III), U(IV), U(V), and U(VI) when, mobile forms in groundwater contain the bivalent uranyl ion, UO_2^{2+}, with the metal in its highest oxidation state[1,3]. In the literature there are a lot of U(VI) ions determination procedures [4–30], but there is still great demand for decreasing the detection limit.

Adsorptive stripping voltammetry (AdSV) is a powerful technique for determination of low levels of heavy metal ions, such as uranium. The technique is based upon adsorptive accumulation of metal ions complexed with a suitable ligand at the electrode and then scanning the potential of the electrode in the negative direction. The first procedures were developed using hanging mercury drop or mercury film electrodes [16–28]. In the last years new alternative electrode materials were highly desired because of the toxicity of mercury. Recently we proposed and optimized in a previous publication the procedure for the analysis of uranium by AdSV with cupferron as a complexing agent using a lead film electrode as a good alternative to mercury electrodes [30].

In the present study aimed to obtain a lower detection limit of U(VI) determination, we used the voltammetric electrode cell with two built-in working electrodes that differed significantly in their surface area. The lead film prepared in situ was used in the working electrodes. The lead electrodes were used as they offer the low detection limit as compared to recently proposed mercury free electrodes [31–35]. Additionally the analyte accumulated at such electrodes can be easily transferred to a solution simultaneously with lead film stripping.

The idea of the proposed procedure was as follows. At first the accumulation of the U(VI)-cupferron complex on the large lead film electrode was carried out from the stirred solution. After this step the large electrode was placed very near the electrode with a small surface area (an ensemble of microelectrodes) and U(VI) was stripped from the large electrode. Thus U(VI) accumulated on the large electrode went to the solution directly at the surface of microelectrodes. Next the accumulation of U(VI) on microelectrodes was performed from the non-stirred solution containing U (VI) at a much higher concentration than that of the starting solution. At the end the voltammogram was recorded with uranium signal proportional to its concentration. In the optimized

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conditions the application of the double accumulation step onto two lead film electrodes in one measurement enabled a decrease of the detection limit by over one order of magnitude from 2×10^{-10} mol L^{-1} (obtained using the classical lead film working electrode) [30] to 1.1×10^{-11} mol L^{-1}.

The proposed method was successfully validated using certified reference material seawater NASS-5. This is another advantage of the proposed technique, as the estimation of uranium in seawater is a difficult task because of very low concentration of uranium and a high salt content of seawater [36].

2. Experimental

2.1. Apparatus

Adsorptive stripping voltammetric measurements were carried out with a μAutolab analyzer (Utrecht, The Netherlands). The four-electrode voltammetric cell of 30 mL volume consisting of two working electrodes, a Pt electrode and an Ag/AgCl reference electrode was used. As a working electrode with a large surface area a GC electrode with 12 mm diameter was used. The electrode with a small surface area was an ensemble of five carbon composite microelectrodes.

2.2. Construction of the voltammetric cell and measuring procedure

A schematic diagram of the proposed new cell containing two working electrodes is shown in Fig. 1 A and B. The position of the first electrode was different in the course of the first and second accumulation step. Briefly, in the course of accumulation of U(VI)-cupferron complex the first electrode was placed about 15 mm above the bottom of the cell. Magnetic stirring bar was used for transport of the complex to the electrode. As the accumulation step at the first electrode was finished the electrode was moved to a short distance near the second working electrode. To control the distance between two working electrodes Teflon foil 0.1 mm thick was placed between the electrode body and the Teflon ring as shown in Fig. 1 A and B. In order to guarantee electrical contact between the electrodes the channel with a 1 mm high triangular cross-section was drilled under the O-ring placed on the casing of the first electrode. The carbon-epoxy microelectrode ensemble was constructed by modification of the procedure proposed in [37]. The composite was obtained by mixing: carbon nanofibers (6.5%), glassy carbon spherical powder of a diameter of 2–12 μm (36%) and epoxy resin. The resulting paste was put under pressure in glass capillary of diameter 25 μm. The capillary filled with carbon-epoxy composite was cured at temperature 110 °C for two days. Five such prepared capillaries were used for construction of the ensemble. Graphite powder was used for the connection between microelectrodes and copper wire.

2.3. Reagents

A standard solution of U(VI) of concentration of 10^{-2} mol L^{-1} was prepared from $(CH_3COO)_2UO_2 \cdot 2H_2O$ by dissolution of reagent in 0.1 mol L^{-1} HNO_3. Cupferron (N-nitrosophenylhydroxylamine ammonium salt) was obtained from Merck. A solution of 1×10^{-2} mol L^{-1} of cupferron was prepared every day by dissolving 0.0155 g of the reagent in water in a 10 mL volumetric flask. The acetate buffer (1 mol L^{-1}) was prepared from Suprapur CH_3COOH and NaOH obtained from Merck. Certified reference material, seawater NASS-5 was obtained from the National Research Council, Canada. Other reagents were obtained from POCh, Poland. All solutions were prepared using triply distilled water. Carbon nanofibers (iron-free) and glassy carbon spherical powder were obtained from Aldrich. Epoxy resin Araldite F and hardener HY 905 were used for fabrication the ensemble of microelectrodes.

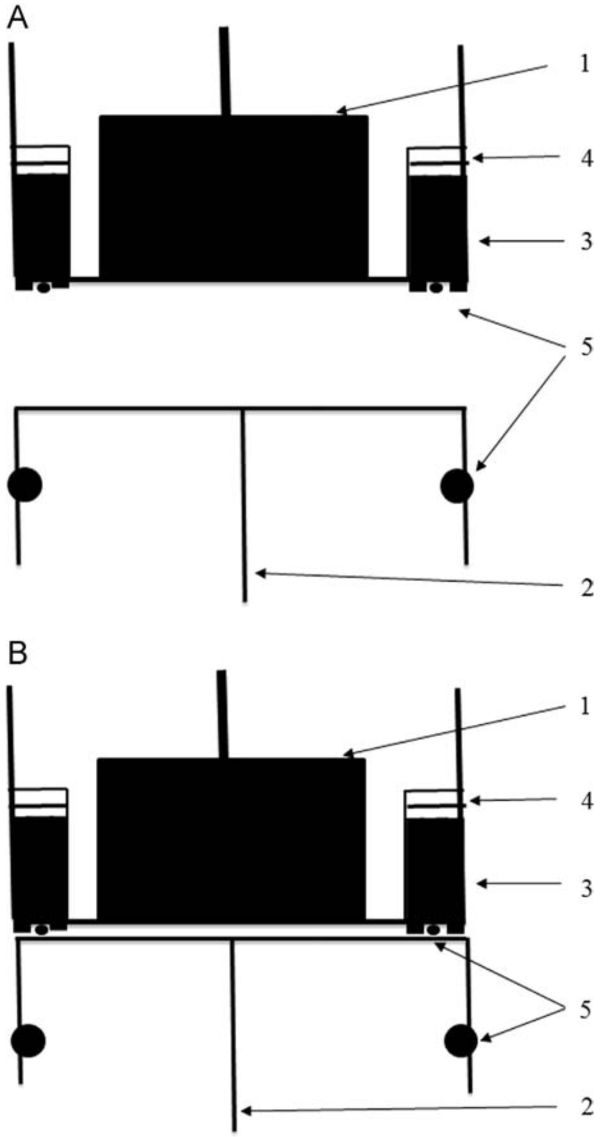

Fig. 1. Schematic diagram of position of electrodes: (A) during the preconcentration step at the first electrode, (B) during the next steps of measurement. 1—the first working electrode; 2—the second working electrode; 3—Teflon ring; 4—Teflon foil; 5—O-rings.

2.4. Certified reference material preparation

Mineralization of certified reference material seawater NASS-5 water sample was performed by UV-irradiation for 3 h. To speed up the process 10 μL of 30% H_2O_2 was added to 10 mL of the sample.

2.5. Voltammetric procedure

The standard measurement was performed in the following way. The 30 mL of the solution containing the analyzed sample, 0.2 mol L^{-1} acetate buffer pH=4.2, 6×10^{-5} mol L^{-1} cupferron, 2.5×10^{-5} mol L^{-1} Pb(II) was pippeted to the voltammetric cell. At first the lead film was formed in situ on the working electrode with a large surface area at −1.1 V for 120 s and next the accumulation of U(VI) on the lead film electrode was carried out at −0.7 V for 120 s from the stirred solution. Stirring was performed using a magnetic stirring bar. After those steps the large electrode was placed near the electrode with a small surface area (an ensemble of microelectrodes) and U(VI) was stripped simultaneously with lead film at the potential of 0 V within 40-s. Thus U(VI) accumulated on the large electrode went to the solution directly at the surface of microelectrodes. Thereupon microelectrodes had contact with the solution containing U(VI) at a much higher concentration as compared with the starting solution. Next the lead film was formed in situ on microelectrodes at -1.1 V for 30 s and the accumulation of U(VI) on this film was carried out at -0.7 V for 120 s from the non-stirred solution enriched with U(VI) ions. Then, after a rest period of 20 s a square wave voltammogram was recorded, while the potential was changed from -0.7 V to -1.4 V. The scan rate and pulse height were equal to 20 mV s^{-1} and -50 mV, respectively. To sum up the accumulation step in the proposed procedure, it was performed two times. The first accumulation was performed on the electrode with a large surface area followed by transition of the accumulated uranium to the solution directly at microelectrodes, so that the second accumulation step on microelectrodes was performed from the solution enriched with U(VI). Due to double accumulation the detection limit was significantly decreased.

3. Results

3.1. Composition of the supporting electrolyte

The 0.2 mol L^{-1} acetate buffer pH=4.2 and 6×10^{-5} mol L^{-1} cupferron were used as supporting electrolyte on the basis of literature data as the most suitable for the U(VI)-cupferron complex accumulation on the lead film electrode [30].

3.2. Conditions of lead film formation

The potential of lead film deposition equal to -1.1 V was chosen on the basis of literature data [30]. The important parameters that drastically influenced the U(VI) signal were Pb(II) concentration and time of accumulation, so those parameters were examined.

The influence of the concentration of Pb(II) used for film formation on the current of the U(VI) peak was studied for the solution containing 0.2 mol L^{-1} acetate buffer, 6×10^{-5} mol L^{-1} cupferron, 1×10^{-9} mol L^{-1} U(VI) and the concentration of Pb(II) was changed in the range from 1×10^{-6} to 2×10^{-4} mol L^{-1}. The obtained results are presented in Fig. 2. The measurements were performed for constant time of lead film formation at the large electrode for 120 s and at microelectrodes for 30 s. The peak current of uranium increases with the increase of Pb(II) concentration and reaches a maximum at a concentration equal to 2.5×10^{-5} mol L^{-1} and at higher concentrations a gradual decrease of the peak current of uranium was observed. Taking into consideration the above results, Pb(II) concentration equal to 2.5×10^{-5} mol L^{-1} was chosen for the whole study.

Next, the influence of the time of lead film formation on the current of the U(VI) peak was studied. The measurements were performed for constant time of lead film formation at microelectrodes (for 30 s) with the time of lead film formation at the large electrode changing from 10 s to 300 s. The obtained results are presented in Fig. 3. The measurements were performed for two different concentrations of U(VI) 5×10^{-10} and 1×10^{-9} mol L^{-1}. It was observed that the peak of uranium increased with the time of lead film formation to 120 s for higher concentration of uranium, and to 150 s for lower concentration of uranium. For standard measurements the time of film formation on the large electrode equal to 120 s was chosen.

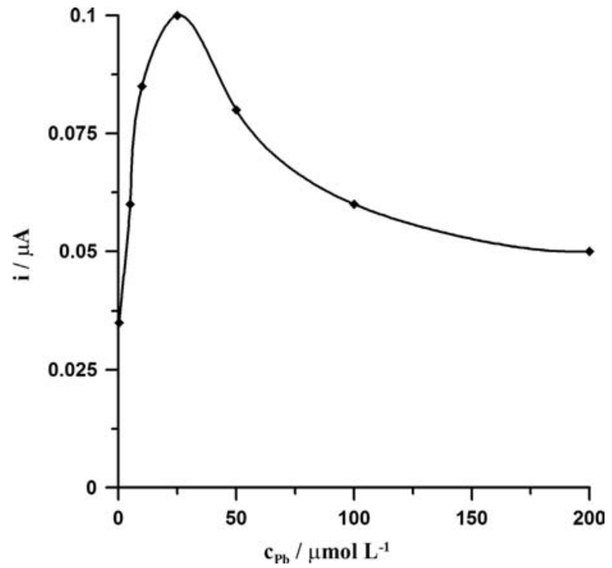

Fig. 2. The influence of Pb(II) concentration on the U(VI) peak current for a solution containing 0.2 mol L^{-1} acetate buffer, 6×10^{-5} mol L^{-1} cupferron, 1×10^{-9} mol L^{-1} U(VI).

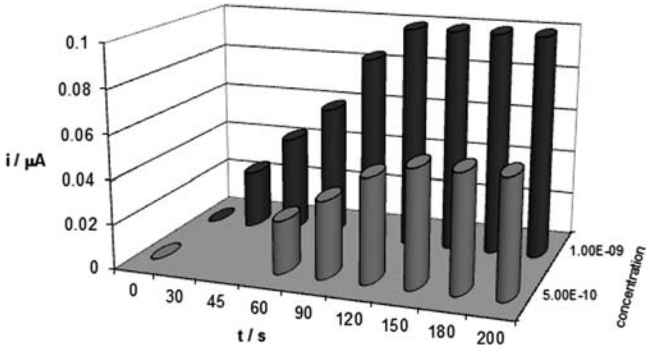

Fig. 3. The influence of time of lead film formation on the 1×10^{-9} mol L^{-1} U(VI) and 5×10^{-10} mol L^{-1} U(VI) peak current.

Next the measurements were performed for constant time of lead film formation at large electrodes (120 s) with the time of lead formation at microelectrodes changing from 10 s to 60 s. The measurements were performed for two different concentrations of U(VI) 5×10^{-10} and 1×10^{-9} mol L^{-1}. It was observed that the peak of uranium increased with the time of lead formation only to 30 s for both concentrations of U(VI). For standard measurements, the time of film formation on microelectrodes equal to 30 s was chosen.

3.3. Conditions of U(VI)-cupferron accumulation

The potential of accumulation of the U(VI)-cupferron complex on the lead film electrodes equal to -0.7 V was selected on the basis of literature data as the most suitable [30].

The accumulation time of the complex on the working electrode is one of the parameters that have a pronounced effect on sensitivity in stripping voltammetry procedures. The effect of the accumulation time on 5×10^{-10} mol L^{-1} U(VI) peak current was examined for constant accumulation time on the lead film microelectrodes (120 s) when accumulation time on the large lead film electrode was changing from 30 s to 600 s. The value of the voltammetric peak current was found to increase with accumulation time to 480 s and then, during a longer time, it progressively decreased.

Next the measurements were performed for constant accumulation time of the U(VI)-cupferron complex on the large lead film

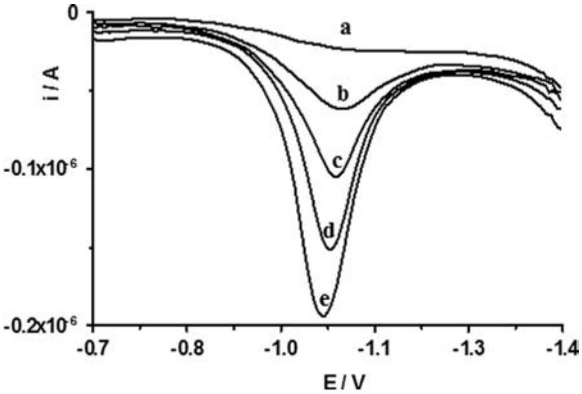

Fig. 4. Voltammograms obtained during the U(VI) determination in NASS-5 certified reference material: (a) blank; (b) NASS-5 diluted 20 times; (c) as (b)+ 5×10^{-10} mol L^{-1} U(VI); (d) as (b)+ 1×10^{-9} mol L^{-1} U(VI); (e) as (b)+ 1.5×10^{-9} mol L^{-1} U(VI).

electrode (120 s) when accumulation time of the complex on the lead film microelectrodes was changing from 30 s to 480 s. It was observed that the value of the voltammetric peak currents increased with accumulation time to 240 s and then, during a longer time, it remained constant.

3.4. *Calibration graphs*

The calibration graphs were obtained for shorter and longer accumulation time of U(VI) on lead film electrodes. The calibration graph for the accumulation time of 120 s on the large electrode and 120 s on microelectrodes was linear in the range from 1×10^{-10} to 5×10^{-9} mol L^{-1} and obeyed the equation $y = 106x - 2.5$, where y and x are the peak current (nA) and U(VI) concentration (nmol L^{-1}), respectively. The linear correlation coefficient was $r = 0.998$. The relative standard deviation for U(VI) determination at concentration 5×10^{-10} mol L^{-1} was 5.3% ($n = 5$). The detection limit estimated from three times the standard deviation of low U (VI) concentration was about 3.1×10^{-11} mol L^{-1}.

The calibration graph for the accumulation time of 480 s on the large electrode and 240 s on microelectrodes was linear in the range from 5×10^{-11} to 2×10^{-9} mol L^{-1} and obeyed the equation $y = 329x - 1.1$, where y and x are the peak current (nA) and U(VI) concentration (nmol L^{-1}), respectively. The linear correlation coefficient was $r = 0.997$. The relative standard deviation for U(VI) determination at concentration 2×10^{-10} mol L^{-1} was 6.2% ($n = 5$). The detection limit estimated from three times the standard deviation of low U(VI) concentration was about 1.1×10^{-11} mol L^{-1}.

3.5. *Interferences*

The determination of U(VI) at concentration 5×10^{-10} mol L^{-1} is not influenced by 100-fold excess of Cu(II), Zn(II), Fe(III), Ni(II), Co(II), Mn(II), Al(III), V(V) and 10-fold excess of Mo(VI). It was found that a 20-fold excess of Mo(VI) causes a decrease of the Mo (VI) signal to 60% of its original value.

3.6. *Analytical validation*

The proposed procedure with double accumulation step was validated in the course of U(VI) determination in water certified material seawater NASS-5. Determinations were performed using the method of standard additions. The result obtained (2.42 μg L^{-1}) with RSD 4.8% ($n = 3$) was in agreement with the information value reported by the producer (2.6 μg L^{-1}). Voltammograms obtained in the course of U(VI) determination in NASS-5 certified reference material are presented in Fig. 4. The good agreement between the result obtained for reference material with information value reported by the producer allowed us to state that the proposed procedure can be applied to U(VI) determination in natural water samples. It should be emphasized that the estimation of uranium in seawater is a difficult task because of very low concentration of uranium and a high salt content of seawater [31].

4. Conclusions

It was concluded that the use of double accumulation step on two lead film electrodes in one measurement in order to decrease the limit of detection of U(VI) was a good idea. The proposed optimized procedure is simple and more sensitive than the other existing voltammetric procedures. The measurements were carried out without removing the oxygen from solutions, which additionally simplified and shortened the time of the analysis. This method is suitable for determining very low levels of uranium in real samples such as environmental water samples.

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