A Miniaturized System for Ultratrace Uranium Analysis in Waters

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Abstract

In this work, a new miniaturized system was developed for uranium detection in waters using adsorptive stripping voltammetry associated with square wave measurements (SWAdSV). The uranium-propy gal late (U-PG) complex accumulated at -1.4 V deposition potential, and with a 200 s deposition time, when the uranium containing sample was mixed with 0.05 mM PG in 0.05 M sodium acetate buffer (pH 4.2). The results obtained have demonstrated the capacity of the miniaturized system and the SPE microelectrodes to detect uranium, with a detection limit of 0.5 ng/L (n = 6, r² = 0.98), and a dynamic range from 5 ng/L to 10 μg/L, and a sensitivity of 100 nA/μg.

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Keywords: adsorptive stripping voltammetry (AdSV); Uranium; screen-printed microelectrodes

1. Introduction

Uranium is radioactive, toxic and a suspected teratogen. Several countries of the European Union plan to introduce a legal limit for the maximum concentration of uranium in drinking water. While different national health authorities prescribe limits ranging up to 10 μg/L, the World Health Organization (WHO) recommends a concentration limit for uranium of 15 μg/L for daily water consumption of 2 L per day, this limit leaves a considerable safety margin [1-5]. Because uranium is a relatively mobile element in many surface or near-surface environment, its geochemical exploration methods require the measurement of trace quantities of metal ion in water samples along with that in plants, soils, and rocks. The uranium concentration of seawaters is about 3.3 μg/L [6-9] and is even lower in freshwater. Thus, highly sensitive methods are required for preconcentration and determination of uranium in water samples collected for prospecting purposes. Adsorptive stripping voltammetry (AdSV) is a powerful technique for determination of levels (ng/mL) of metal ions and organics [10-12].

In this paper we have developed an alternative method to meet regulatory requirements in using a system miniaturized with an adsorptive stripping voltammetric (AdSV) procedure for determination of uranium in water. The miniaturized system consists of a screen-printed microelectrode chip, a carbon working microelectrode (diameter Ø 1 mm), an integrated Ag/AgCl reference electrode, a platinum counter electrode and a PMMA (polymethylacrylate) 20 μL microcell. This method is based on the effective accumulation of the uranium complexed

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with propyl gallate on a working SPE microelectrode, then reduction of the adsorbed complex. Influence of effective parameters such as pH, concentration of ligand, accumulation potential and accumulation time on the sensitivity and selectivity were studied.

2. Material and Methods

A PalmSens PC system (Eindhoven, the Netherlands) was used to apply pulse techniques to the carbon electrodes. It was connected to a PC computer loaded with specific software. The electrodes are screen-printed microelectrodes (SPE) produced by BVT Technologies (Brno, Czech Republic). They are composed of three electrodes: the reference electrode based on powders of silver and silver chloride, the auxiliary electrode based on powder platinum and the working electrode based on graphite powder with a diameter of 1 mm. The SPE electrodes were deposited on a single ceramic chip 0.63 mm thickness and dimensions (25.4 × 7.26 mm). The SPE were placed in a microcell made of PMMA (Polymethylmetacrylate), 20 μL volume and (42 × 24 × 16 mm) dimensions, commercialized by BVT Technologies (Brno, Czech Republic). With this microcell, no agitation and no degassing of the solution were applied.

Square Wave Adsorptive Stripping Voltammetry (SWAdSV) was used for all experiments. The experimental conditions for the determination of uranium-propyl gallate (U-PG) complex in the system miniaturized are presented in Table 1.

| Table 1: Experimental conditions for the determination of uranium using SWAdSV with miniaturized system |
|---------------------------------------------------|---------------------------------------------------|
| Potential scan                                    | From -0.8 V to 0 V                                 |
| Scan rate                                         | 0.01 V/s                                          |
| Potential step                                    | 0.01 V                                            |
| Pulse duration                                    | 0.01 s                                            |
| Time of adsorption                                | 200 s                                             |
| Potential of adsorption                           | -1.4 V                                            |
| Conditioning potential                            | 0 V                                               |
| Electrolyte buffer                                | 0.05 mM PG in 0.05 M acetate buffer (pH = 4.5)     |

3. Results and Discussion

3.1. Influence of adsorption potential and time
The influence of the adsorption potential was studied for uranium concentration of 1 μg/L, in 0.05 M acetate buffer (pH 4.2) containing 0.05 mM propyl gallate. The adsorption potential was changed from −0.5 to −1.6 V for 90 s of deposition time. It was observed that the current of the uranium peak increases as the potential changes from −0.5 to −1.4 V and then slowly decreases. For further study an accumulation potential −1.4 V was chosen (Fig. 1).

The effect of adsorption time of U-PG complex was studied using concentration of uranium of 1 μg/L in 0.05 M acetate buffer (pH 4.2) containing 0.05 mM propyl gallate for -1.4 V potential, after different accumulation time (60-300 s). It was observed that the current of the peak increases linearly with the accumulation time up to 200 s. For further study the accumulation time of 200 s was chosen. For determinations of lowest uranium concentrations an increase of the accumulation time is recommended.

3.2. Effect of propyl gallate concentration
The concentration of the propyl gallate was changed from 5 to 100 μM, and its influence on the uranium peak current was studied. The peak current for U(VI) increases as propyl gallate concentration increases to 50 μM and then is nearly stable so for further studies, propyl gallate concentration 50 μM was chosen.
3.3. Effect of pH and buffer concentration
An acetate buffer was used as the main component of the electrolyte on the basis of literature data [12]. The pH of the solution was changed from 2 to 6. On the basis of these results the pH 4.2 ± 0.1 was chosen for further studies. Next the concentration of the acetate buffer was changed and its influence on the uranium signal was studied. It was found that the current of the uranium peak increases as the concentration of the acetate buffer increases to 0.05 M and then slowly decreases. For further study concentration of the buffer 0.05 M was chosen.

3.4. Calibration curve for uranium detection
The results obtained have demonstrated the capacity of the miniaturized system and the SPE electrodes to detect uranium, with a detection limit of 0.5 ng/L (n = 6, \( r^2 = 0.98 \)), and a linear range from 5 ng/L to 10 μg/L. The reduction peak current of uranium complex was found to be directly proportional to the uranium concentration for sensitivity of 100 nA/μg following 200 s of accumulation (Fig. 2).

3.5. Study of interfering species
In general, AdSV is known as a very sensitive method for the determination of metals through their adsorbable complex. Depending on the selectivity of the complexing reagent the determinations are more or less interfered by other cations. Coexisting metal ions may compete for the ligand binding, thus influencing the uranium response. The influence of the complexing agents was studied by adding EDTA at the concentration 0.01 M. PG result in high selectivity, with no interference in the presence of 1 μg/L of cadmium, copper, lead, zinc, cobalt and iron. In contrast, additions of 10 μg/L of cadmium, copper, zinc, cobalt, iron and lead resulted in a 25%, 75%, 15%, 50%, 40% decrease and 20% increase, respectively of the original value of U-PG peak.
4. Conclusion

Uranium forms a complex with propyl gallate. This complex can be used for a highly sensitive and selective determination of uranium. The above results demonstrate the suitability of SPE electrodes for adsorptive stripping voltammetric (SWAdSV) measurements of trace uranium. The protocol has been optimized by examining the influence of the solution conditions (pH, acetate buffer and propyl gallate concentration), and accumulation parameters (time and potential). The obtained detection limit is lower than the results found in the literature. A major advantage of the proposed method is its high tolerance of co-existing metals as cadmium, copper, lead, zinc, cobalt and iron for low elements concentration. The high performances obtained with SPE microelectrodes, presenting non toxicity, is extremely attractive for on-site environmental and industrial measurements of uranium.

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