

## ANALYSIS OF SILVER IONS BY STATIONARY AND FLOW ELECTROCHEMICAL TECHNIQUES ON THE SURFACE OF GLASSY CARBON ELECTRODE

Radka Mikelová<sup>a, b</sup>, Vojtěch Adam<sup>a, b</sup>,  
Libuše Trnková<sup>c</sup>, Petr Babula<sup>d</sup>, Aleš Horna<sup>e, f</sup>,  
René Kizek<sup>a</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, Faculty of Agronomy, Mendel University of Agriculture and Forestry, Zemědělská 1, CZ-613 00 Brno, Czech Republic

<sup>b</sup> Department of Analytical chemistry, and <sup>c</sup>Department of Theoretical and Physical Chemistry, Faculty of Science, Masaryk University, Kotlářská 37, CZ-611 37 Brno, Czech Republic

<sup>d</sup> Department of Natural Drugs, Faculty of Pharmacy, University of Veterinary and Pharmaceutical Sciences, Palackého 1-3, CZ-612 42 Brno, Czech Republic

<sup>e</sup> Department of Food Engineering and Chemistry, Faculty of Technology, Tomas Bata University, Náměstí T. G. Masaryka 275, CZ-762 72 Zlín, Czech Republic

<sup>f</sup> RADANAL Ltd. Okružní 613, CZ-530 03 Pardubice, Czech Republic  
e-mail: kizek@sci.muni.cz

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### ABSTRACT

It is common knowledge that silver ions belongs to one of the most toxic elements causing acute toxicity of organisms e.g. fifty percent living organisms die after exposition of 10 µg/l Ag<sup>+</sup> per 96 hours. Here we applied two different electrochemical techniques (differential pulse voltammetry and flow injection analysis with electrochemical detection) for determination of silver ions. As we shown, not only the stationary electrochemical technique but also the flow injection analysis in connection with electrochemical detector are suitable for toxicological analysis of environmental samples.

### INTRODUCTION

The effects of silver in the environment have been intensively studying. Existence of International researches organisation such as Silver Coalition (1991-1995) and The Silver Council (from 1996 up to present; <http://www.silvercouncil.org/html/default.htm>) proves this fact. These organisations also established International Conference on Transport, Fate and Effects of Silver in the Environment<sup>1</sup>. Silver ions come to the environment, first of all, from industry. The highest amounts of silver

are used in photographic industry (more than 40 %), in electrotechnical industry (about 30 %), in electrochemical plating (production of jewellery, more than 22 %), in chemical industry (more than 6 %) and in health service (silver amalgam, about 2 %). In addition, amounts of silver ions in waste waters represents the greatest source of their entering to food chain<sup>2</sup>. Moreover, marked toxicity of silver ions has been described<sup>2-10</sup>.

A quantification of silver ions in water is very difficult because there are formed numbers of silver complexes with inorganic and organic compounds, which marked decrease toxicity of silver<sup>1, 11, 12</sup>. A determination of silver ions is obviously performed by atomic absorption spectrometry<sup>13, 14</sup>. It is necessary to preconcentrate a real sample for sensitive analysis, but this process is time consuming and high cost procedure<sup>14-16</sup>. On the other hand electrochemical techniques are able to determine a silver on carbon electrodes at nanomolar concentrations without preconcentration<sup>17-21</sup>.

The aim of this work was to analyse the silver ions by the flow and stationary electrochemical techniques on the surface of the glassy carbon electrode.

### MATERIAL AND METHODS

#### *Chemicals*

Silver nitrate and sodium acetate was purchased from Sigma Aldrich (St. Louis, USA). Acetic acid was purchased from Fluka chemie AG (USA). All reagents used were ACS purity. Stock standard solutions were prepared by ACS water (Sigma-Aldrich, USA). Working standard solutions were prepared daily by dilution of the stock solutions. All solutions were filtered through a 0.45 µm teflon filter discs (MetaChem, Torrance, CA, USA) prior to HPLC analysis. The pH value was measured using WTW inoLab Level 3 with terminal Level 3 (Weilheim, Germany), controlled by the personal computer program (MultiLab Pilot; Weilheim, Germany). The pH-electrode (SenTix-H, pH 0-14/3M KCl) was regularly calibrated by set of WTW buffers (Weilheim, Germany).

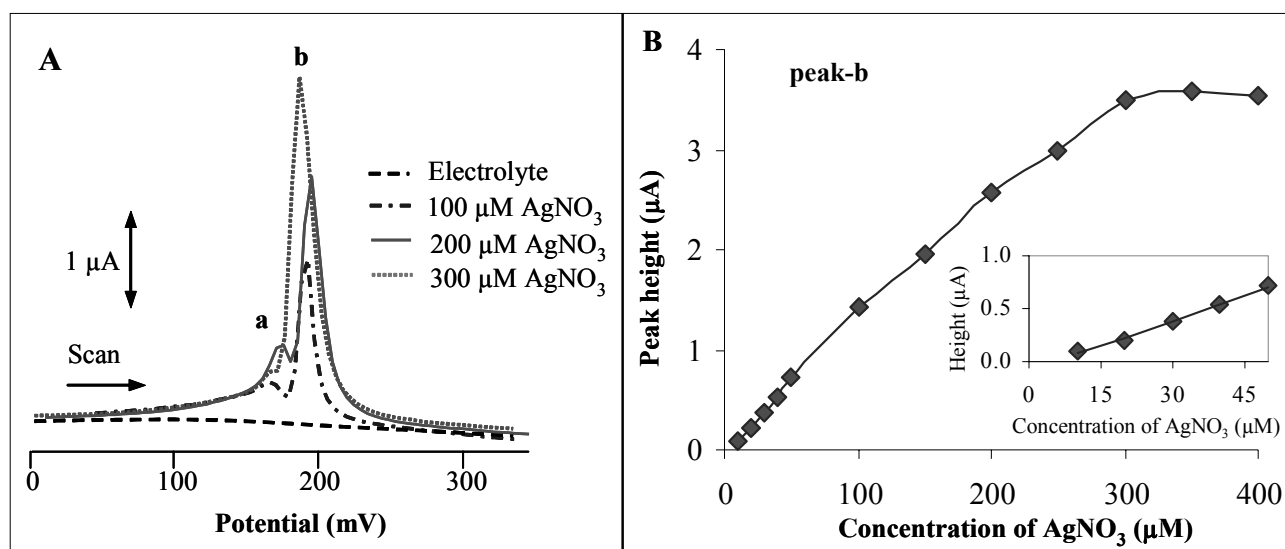
#### *Electrochemical stationary analysis*

Differential pulse voltammetric (DPV) measurements were performed with AUTOLAB Analyser (EcoChemie, Netherlands) connected to VA-Stand 663 (Metrohm, Switzerland), using a standard cell with three electrodes. The working electrode was a glassy carbon electrode. The reference electrode was an Ag/AgCl/3M KCl electrode and the auxiliary electrode was a graphite electrode. For smoothing and baseline correction the software GPES 4.4 supplied by EcoChemie was employed. The supporting electrolyte (0.2 M acetate buffer, pH 5.0) was prepared by mixing buffer components. The DPV measurements were carried out at room temperature. DPV parameters were as follows: an initial potential of -1.2 V, an end potential 1.2 V, a modulation time 0.02 s, a time interval 0.2 s, a step potential of 5 mV/s, a modulation amplitude of 250 mV.

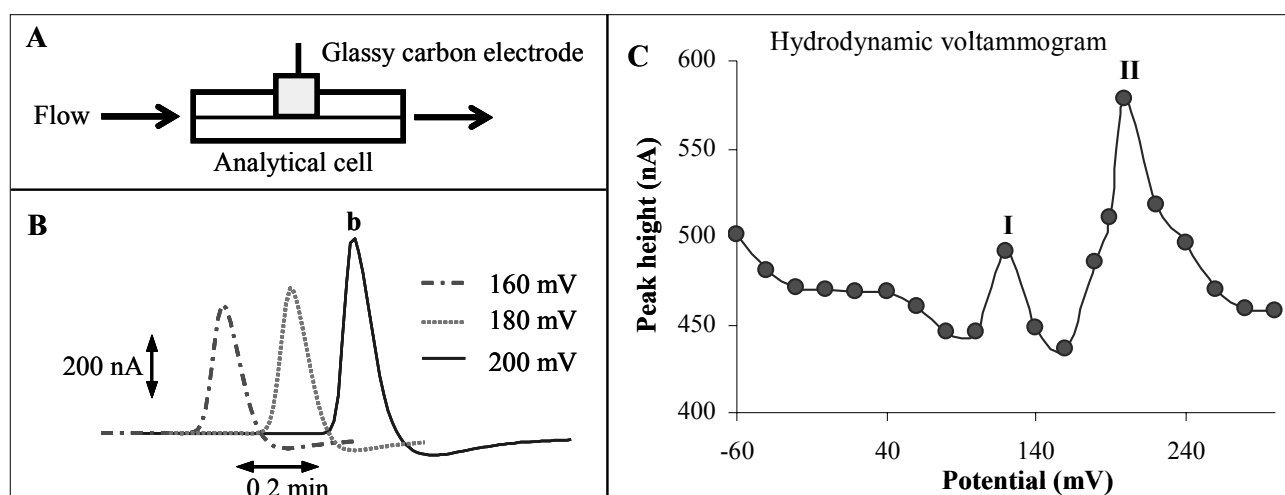
### Electrochemical flow analysis

An flow injection analysis with electrochemical detection FIA ED system consisted of solvent delivery pump (Model 583 ESA Inc., Chelmsford, MA, USA), a guard cell (Model 5020 ESA, USA), a reaction coil (1 m), and an electrochemical detector. The electrochemical detector (ED) includes one low volume flow-through amperometric analytical cells (Model 5040, ESA, USA), which is

consisted of glassy carbon working electrode, palladium electrode as reference electrodes and auxiliary carbon electrode, and Coulochem III (ESA Inc. Chelmsford, MA, USA) as a control module. The working electrode was purified by setting of potentials of  $-1000/+1000$  mV. The sample ( $5 \mu\text{l}$ ) was injected manually. The obtained data were treated by CSW 32 software. The experiments were carried out at room temperature.



**Fig. 1.** Electrochemical stationary analysis. Typical DPV voltammograms of 100, 200 and 300  $\mu\text{M}$  of  $\text{AgNO}_3$  (A). Dependence of peak *b* height on concentration of silver ions in the range of 0–400  $\mu\text{M}$  (B) and in the range of 0–50  $\mu\text{M}$  (inset in B). The supporting electrolyte (0.2 M acetate buffer, pH 5.0) was prepared by mixing buffer components. DPV parameters were as follows: supporting electrolyte of 0.2 M acetate buffer (pH 5.0), an initial potential of  $-1.2$  V, an end potential 1.2 V, a modulation time 0.02 s, a time interval 0.2 s, a step potential of 5 mV/s, a modulation amplitude of 250 mV.



**Fig. 2.** Electrochemical flow analysis. The simplified scheme of flow-through analytical cell (A). Typical FIA-ED chromatograms of silver ions at three different potentials of working electrode (B). Dependence of the silver ions peak height on the potential of the glassy carbon electrode – hydrodynamic voltammogram (C). The FIA ED parameters were as follows: mobile phase of 0.2 M acetate buffer (pH 5.0), flow rate  $0.8 \text{ ml}\cdot\text{min}^{-1}$ , potential guard cell 0 V, filter 2 sec, current 20  $\mu\text{A}$ , sample injection 5  $\mu\text{l}$ .

## RESULTS AND DISCUSSION

Primarily the silver ions were analysed by differential pulse voltammetry (DPV) on the surface of glassy carbon electrode. We observed two signals: i) peak *a* at potential of 0.16 V and ii) peak *b* at potential of 0.19 V (Fig. 1A). The voltammetric signals *a* and *b* changed according to different concentration of silver ions, but we selected peak *b* for analytical purposes. Changes in peak *b* height with increasing concentration of silver ions are shown in Fig. 1B. If the concentration of silver ions exceeded 300  $\mu\text{M}$ , the changes of peak *b* height was very low. This phenomenon relates with perfect coverage of the surface of the working electrode. In addition the concentration dependence of silver ions (0–50  $\mu\text{M}$ ) was strictly linear:  $y = 0.0158x - 0.0873$ ;  $R^2 = 0.9953$  (Fig. 1B). It is evident from the obtained results that it is possible to detect the silver ions on the surface of glassy carbon electrode.

A flow electrochemical determination (flow injection analysis; FIA) of silver ions was selected due to analysis of environmental samples. The simplified scheme of flow-through analytical cell used in our experiments is shown in Fig. 2A. We observed well separated signal of silver ions (Fig. 2B). On the base of the obtained results from stationary system, we selected the range of potentials used for plotting of hydrodynamic voltammogram. To be specific, we applied the potential ranged from –60 mV to +300 mV. We observed two maximums (I and II) on the hydrodynamic voltammogram (Fig. 2C). The first maximum (I) was obtained at potential of 120 mV and the second at potential of 200 mV (Fig. 2C). As we shown, the flow injection analysis in connection with electrochemical detector is suitable for toxicological analysis of environmental samples.

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