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## Electrochemical sensor based on phospholipid modified glassy carbon electrode - determination of paraquat

H. Tomková<sup>a</sup>, R. Sokolová<sup>b</sup>, T. Opletal<sup>a</sup>, P. Kučerová<sup>a</sup>, L. Kučera<sup>a</sup>, J. Součková<sup>a</sup>, J. Skopalová<sup>a,\*</sup>, P. Barták<sup>a</sup>

<sup>a</sup> Regional Centre of Advanced Technologies and Materials, Department of Analytical Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, 771 46 Olomouc, Czech Republic

<sup>b</sup> J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Prague 8, Czech Republic

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### ABSTRACT

Electrochemical sensor based on glassy carbon electrode modified with asolectin (mixture of soybean phospholipids) was developed. Properties of phospholipid layer, such as thickness and compactness, were investigated using atomic force microscopy and X-ray photoelectron spectroscopy. Phospholipids completely cover whole surface and the thickness of the layer  $7.1 \pm 1.2$  nm corresponds to the value of the phospholipid bilayer of cell membranes. Due to the accumulation of paraquat in the phospholipid layer, square wave voltammetry with asolectin modified electrode exhibits three times higher sensitivity, measured as a slope of calibration dependence, and better linearity in comparison to unmodified glassy carbon electrode. Limit of detection  $2.2 \text{ nmol L}^{-1}$  and recoveries higher than 88% were achieved in model samples of water. The method was used for determination of paraquat in real sample of river water and results were compared with high performance liquid chromatography and differential pulse voltammetry on hanging mercury drop electrode giving  $0.071 \pm 0.010$ ,  $0.050 \pm 0.010$  and  $0.061 \pm 0.008 \text{ } \mu\text{mol L}^{-1}$ , respectively.

### 1. Introduction

Self-assembled lipid bilayers on solid electrodes are used as simple models to mimic biological cell membranes for many years. This type of bilayer lipid membranes (BLMs) was used for the first time by Tien and Salamon in 1989 [1]. Since the time, various materials such as silver [2], gold [3], mercury [4], glassy carbon [5] and other matter [6] were employed as supports for phospholipid layers. Solid supported BLMs have been applied for characterization of membrane structure [7,8], drug-membrane [9,10] and protein-membrane interactions [11]. Properties of phospholipid layers were studied by various methods, including cyclic voltammetry (CV) [12,13], electrochemical impedance spectroscopy (EIS) [14], atomic force microscopy (AFM) [15] or nuclear magnetic resonance (NMR) [16].

The supported lipid structures are capable to accumulate organic molecules, depending on their charge and hydrophilic-lipophilic balance. Wide range of biologically active substances such as drugs, peptides and pesticides interact with lipids and fatty acids leading to accumulation of the lipophilic compounds. The feature can be advantageously employed in phospholipid modified electrodes to improve selectivity and sensitivity in detection of many biologically

significant substances [17]. For example, carbon paste electrode (CPEs) modified with phospholipids and fatty acids were used for pre-concentration and determination of drugs promethazine [18], epirubicin and adriamycin [19], ceftioxiem [20], marcellomycin [21], trimipramine [22], piroxicam and tenoxicam [23].

Accordingly, many articles, e.g [2,3,5,6], describe the preparation of phospholipid bilayer on the surface of solid electrodes, including glassy carbon electrode (GCE). However, pure phospholipids are used to prepare analytically acceptable membrane. By contrast, principal aim of this communication consists in preparation and characterization of the phospholipid membrane from the relatively cheap mixture of crude soybean phospholipids, commercially available as asolectin, and its application for the same purpose. To the best of our knowledge, chemical composition as well as self-assembled structure of such membrane better mimic real biomembranes. Electrochemical sensor based on asolectin modified glassy carbon electrode and square-wave voltammetric method for sensitive determination of pesticide paraquat is described in this contribution as a proof of principle.

Paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride; methyl viologen; Gramoxone) is one of the broad spectrum, non-selective and quick-acting contact herbicides [24,25], destroying plant cells by

\* Corresponding author.

E-mail address: [jana.skopalova@upol.cz](mailto:jana.skopalova@upol.cz) (J. Skopalová).

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interfering with photosynthetic electron transfer systems [26]. Its application is forbidden in the European Union [27] for its toxicity to mammals [28–30] ( $LD_{50, human}$  35 mg kg<sup>-1</sup>,  $LD_{50, rat}$  110–150 mg kg<sup>-1</sup>) [31], however it is still used in about 130 other countries [32]. For the reason, methods for the paraquat analysis are constantly developed since its introduction in 1962, including HPLC with diode array detector [33,34], HPLC/MS [35], HPLC/MS/MS with positive ion electrospray ionization [36,37], GC/MS [38], Raman spectroscopy [39,40], UV–Vis spectrophotometry [41,42], square wave voltammetry [32,43], differential pulse voltammetry [44,45], spectrofluorimetry [46] and ELISA [47,48].

Carbon paste electrodes (CPEs) with different type of modifiers reaching limits of detection (LOD) of paraquat residues on nanomolar level were described formerly [32,49–53]. Our previous study was aimed at investigation of asolectin properties and development of CPE sensor modified with asolectin for determination of paraquat in water with LOD 200 nmol L<sup>-1</sup> [54]. Over and above, permeability and fundamental properties of asolectin self-organized layer on GCE were tested with cyclic voltammetry and AC impedance spectroscopy as well [54]. However, the results did not lead to the applicable electrochemical sensor consisting of self-assembled asolectin membrane on the solid support. Only advanced investigation of GCE supported phospholipid layer with AFM and X-ray photoelectron spectroscopy (XPS) allowed development of the electrochemical sensor with detection limit improved in almost two orders of magnitude. Results obtained by AFM, as an extraordinary method of the topographical and mechanical characterization of the active surface [15,55,56] and XPS, as an extraordinary method of chemical analysis of the electrode surface and phospholipid layer, and their application in development of novel electrochemical sensor are the main topics of this communication. Square wave voltammetry (SWV) was used to study accumulation of the paraquat in phospholipid layer and to selectively determine paraquat in aqueous samples. The results obtained with SWV in river water were compared with those from high performance liquid chromatography (HPLC) and differential pulse voltammetry (DPV) on hanging mercury drop electrode (HMDE).

## 2. Experimental

### 2.1. Chemicals and reagents

Asolectin from soybean (mixture of phospholipids containing about 25% of phosphatidylcholine) was purchased from Fluka (Buchs, Switzerland). Paraquat perchlorate (methylviologen perchlorate) was precipitated from commercial formulation (Gramoxone) with sodium perchlorate solution, recrystallized from deionized water and dried in vacuum desiccator over phosphorus pentoxide [57]. Hexane, hydrochloric acid, sodium chloride and sodium sulphate (crystalline, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O) were from Lachema (Brno, Czech Republic). Potassium chloride (99.999 Suprapur) was obtained from Merck (Prague, Czech Republic), sulphuric acid and methanol were from Penta (Prague, Czech Republic) and trifluoroacetic acid was from Sigma Aldrich (St. Luis, USA). All reagents were of analytical grade, unless otherwise stated. Deionized water (Millipore, 18.2 MΩ) was used for preparation of all solutions.

### 2.2. Preparation of asolectin modified GCE (LMGCE)

Bare GCE was polished with 0.05 μm alumina slurry on wet microcloth and then ultrasonicated for 2 min in deionized water. The surface was pretreated electrochemically in NaCl solution (9 g L<sup>-1</sup>) at the potential of 1.5 V (vs. Ag|AgCl|3 M-KCl) for 3 min [58], and afterwards it was rinsed with deionized water and dried under argon. Phospholipid layer was formed on the clean, electrochemically pretreated bare GCE surface as follows. Asolectin solution (3 mg mL<sup>-1</sup>) [59] was dropped on the dry surface of GCE and the electrode was

immersed into the NaCl solution (9 g L<sup>-1</sup>) for 30 min. The electrode was then rinsed with deionized water and immediately used for electrochemical measurements or dried under argon prior to AFM and XPS measurements. For AFM measurement solution of KCl (Suprapur grade) of the same concentration was used instead of NaCl.

### 2.3. AFM measurements

The vessels intended for the solution preparation were cleaned by freshly prepared carboxylic acid solution (concentrated sulphuric acid/concentrated hydrogen peroxide, 3:1 v/v), washed by deionized water and dried in the air.

All AFM measurements were carried out *ex situ* on Agilent 5500 SPM (Agilent Technologies, Santa Clara, USA). The measurements employed the rectangular magnetically coated cantilevers (Type II MAClevers) with the nominal resonant frequency 75 kHz and nominal force constant 2.8 N m<sup>-1</sup>. All images were obtained in the tapping mode at the recording speed 0.8 line s<sup>-1</sup>. Besides the topography information, the phase shift between the driving alternating voltage and the amplitude of the probe oscillation were recorded. It represented the complementary qualitative information about the structures on the interfaces. The nanoshaving was performed in the constant-force contact mode with the same AFM probe. The force values calculated using Hooke law were in the range of 640–700 nN. All images were obtained at the resolution 512 pixels. They were processed in software Gwyddion 2.7 (Czech Metrology Institute, Czech Republic). The results from topography (the height of layers etc.) were obtained from software PicoView 1.10.7 (Agilent Technologies) and analyzed in Origin 8 (OriginLab Corporation, Northampton, USA). The topography images shown in Results and discussion are all plane-corrected. Presented values of the roughness and layers thickness obtained from histogram are rounded to one decimal place, which is in agreement with the accuracy limit of the employed AFM configuration.

### 2.4. XPS measurements

Preparation of the clean electrode surface and its pretreatment before formation of phospholipid layer was carried out using three procedures: (i) polishing with 0.05 μm alumina slurry on wet microcloth and ultrasonication in deionized water for 2 min, (ii) polishing with alumina slurry on wet microcloth, ultrasonication in deionized water for 2 min and anodic pretreatment in NaCl solution (9 g L<sup>-1</sup>) at the potential 1.5 V (vs. Ag|AgCl|3 M-KCl) for 3 min and (iii) polishing with alumina slurry on wet microcloth, ultrasonication in deionized water for 2 min and cathodic pretreatment in HCl solution (0.1 mol L<sup>-1</sup>) at the potential -1.5 V (vs. Ag|AgCl|3 M-KCl) for 3 min.

Removing of phospholipid layer and renovation of the electrode surface was performed using above described procedures (i), (iii) and procedure (iv) which involved polishing of the electrode with alumina slurry, ultrasonication in deionized water for 2 min, drying under argon and successive ultrasonic cleaning in hexane, methanol and deionized water, each for 15 min.

The samples (i.e. GCEs treated as given above and LMGCE) were mounted in a sample holder (1 in. in diameter) using the non-fluorine double-sided Scotch tape (3M, St. Paul, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed using the PHI VersaProbe II XPS system (Physical Electronics, Chanhassen, USA) with hemispheric analyzer and monochromatic Al-Kα source (15 kV, 50 W), photon energy of 1486.7 eV. All the spectra were recorded in the vacuum of 1.3 × 10<sup>-8</sup> Pa and at the room temperature of 20 °C. The spot of 200 μm diameter was analyzed in each measurement. The survey scan spectra were acquired with pass energy of 187.850 eV, binding energy (BE) range of 0–1300 eV and electronvolt step of 0.8 eV, while pass energy of 23.500 eV and electronvolt step of 0.2 eV were used for the high-resolution spectra. The dual beam compensation was used for

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