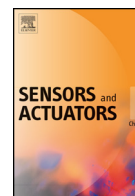


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Polyaniline–DNA based sensor for the detection of anthracycline drugs



Rezeda Shamagsumova^a, Anna Porfireva^a, Veronika Stepanova^a, Yury Osin^b,
Gennady Evtugyn^{a,c}, Tibor Hianik^{c,d,*}

^a Analytical Chemistry Department of Kazan Federal University, 18 Kremlevskaya Street, Kazan 420008, Russian Federation

^b Interdisciplinary Center of Analytical Microscopy of Kazan Federal University, 18 Kremlevskaya Street, Kazan 420008, Russian Federation

^c OpenLab “DNA-Sensors” of Kazan Federal University, 18 Kremlevskaya Street, Kazan 420008, Russian Federation

^d Department of Nuclear Physics and Biophysics, Comenius University, Mlynska dolina F1, 842 48 Bratislava, Slovakia

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ABSTRACT

New approach of the detection of anthracycline preparations intercalating native DNA has been proposed and realized in the assembly of electrochemical sensor. Glassy carbon was covered with polyaniline obtained by electropolymerization in the presence of native DNA and oxalic acid as doping agents. It was shown by impedimetric and voltammetric measurements, the surface coating obtained showed an extended pH range of electrochemical activity and retained ability to interact with specific intercalators. The incubation of the sensor with anthracycline preparations resulted in regular decrease of electrochemical transfer resistance and suppression of redox probe current (ferricyanide anion). In optimal conditions the detection limits of 0.01 nM doxorubicin, 0.1 nM daunorubicin and 0.2 nM idarubicin were achieved. The replacement of oxalic acid with sulfuric acid as polymerization media as well as thermal denaturation of DNA resulted in disappearance of the response. The selectivity of DNA interaction detection was higher in weakly acidic media for impedimetric measurements and in HEPES, pH 7.0, for voltammetric detection. Albumin, blood plasma electrolytes and sulfanyl amides do not interfere with anthracycline measurements. The electrochemical sensor developed was tested in the determination of doxorubicin in commercial preparation with 91–93% recovery.

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1. Introduction

Small molecules able to interact with DNA have found increasing attention in the past decade due to enormous growth of their applications that mainly include visualization of DNA molecules in vitro and inside the cells and antitumor chemotherapy [1]. Many modern antitumor drugs intercalate or modify DNA of cancer cells to prevent their transcription and cancer cell division. Similar effect is exerted on viruses. Intercalation assumes insertion of a planar drug molecule between DNA base pairs followed by distortion of the DNA helix, increasing its own volume and lengthening the DNA molecule [2]. Some intercalators like doxorubicin can also promote DNA damage by activation of the formation of reactive oxygen species, stabilization of DNA cleavage complexes and inhibition of repair systems [3,4]. In spite of high efficiency, most anticancer drugs are very toxic so that the gap between therapeutic and

potentially dangerous dose is rather narrow and highly depends on individual specificity of drug metabolism. For this reason as well as for screening new less toxic pharmaceuticals, new methods are demanded for fast and reliable detection of DNA targeting species.

The detection of DNA–drug intercalation is mainly based on the changes in optical properties of reactants, e.g. red shift of DNA bands in UV–vis spectra [5], changes in circular dichroism of the complexes [6], or excitation of fluorescence of some intercalators (ethidium bromide [7]). Being universal, optical methods are less appropriate for sensor mode and excessively sensitive to matrix interferences affecting the response of target interactions.

Electrochemical DNA-sensors are considered as an alternative to conventional spectroscopic techniques due to lesser cost, high sensitivity of the response, compatibility with conventional measurement equipment, intuitively understandable design and simple measurement mode [8]. Three strategies are utilized for electrochemical detection of antitumor drugs, i.e., (i) recording oxidation of guanine (and to a less extent adenine) residues in the DNA strand [9–12]; (ii) detecting signal referred to electrochemically active drug affected by interaction with DNA [13–16]; and (iii) monitoring changes in the surface layer morphology following

* Corresponding author at: Department of Nuclear Physics and Biophysics, Comenius University, Mlynska dolina F1, 842 48 Bratislava, Slovakia.

Tel.: +421 2 60295683.

E-mail address: tibor.hianik@fmph.uniba.sk (T. Hianik).