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Polyaniline–DNA based sensor for the detection of anthracycline drugs

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ABSTRACT

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

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 reparation 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 individual specificity of drug metabolism. For this reason as w as for screening new less toxic pharmaceuticals, new methods a demanded for fast and reliable detection of DNA targeting speci

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

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

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