



Thin-film electrochemical sensor for diphenylamine detection using molecularly imprinted polymers

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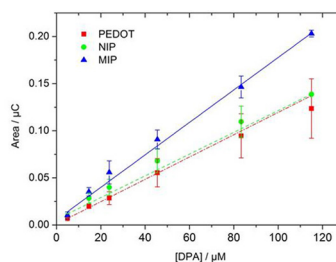
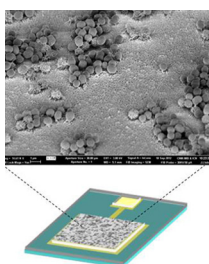
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HIGHLIGHTS

- New voltammetric sensor for diphenylamine detection.
- Thin-film miniaturized electrode modified with a molecularly imprinted polymer.
- Molecularly imprinted particles anchored into an electropolymerised poly(3,4-ethylenedioxythiophene) membrane.
- Analysis of diphenylamine in spiked apple juice samples.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reports on the development of a new voltammetric sensor for diphenylamine based on the use of a miniaturized gold electrode modified with a molecularly imprinted polymer recognition element. Molecularly imprinted particles were synthesized *ex situ* and further entrapped into a poly(3,4-ethylenedioxythiophene) polymer membrane, which was electropolymerized on the surface of the gold electrode. The thickness of the polymer layer was optimized in order to get an adequate diffusion of the target analyte and in turn to achieve an adequate charge transfer at the electrode surface. The resulting modified electrodes showed a selective response to diphenylamine and a high sensitivity compared with the bare gold electrode and the electrode modified with poly(3,4-ethylenedioxythiophene) and non-imprinted polymer particles. The sensor showed a linear range from 4.95 to 115 μM diphenylamine, a limit of detection of 3.9 μM and a good selectivity in the presence of other structurally related molecules. This sensor was successfully applied to the quantification of diphenylamine in spiked apple juice samples.

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1. Introduction

Molecular imprinting has gained popularity during the last decades as a technique of synthesizing polymer materials with

chemically selective recognition sites [1–3]. Molecular imprinting consists in the polymerization of the monomer mixture in the presence of the target molecule or template in an inert solvent. After polymerization, the template is removed from the polymer matrix, thus leaving cavities or specific binding sites in the resulting material that selectively interact with the template molecule and that give rise to molecularly imprinted polymer matrices (MIPs). The high specificity and stability of MIPs as well as the possibility to synthesize polymers for practically any analyte render them attractive artificial ligands or receptors for various analytical applications including chemical sensing [4].

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The use of the MIPs as stationary phases for liquid chromatography [5], sorbents for solid-phase extraction [6,7] and ligand binding assays [8] have been reported. Although less numerous, MIPs have also been applied as recognition elements in various types of sensors, including mass [9], impedimetric [10], amperometric [11] and potentiometric [12–14] sensors, among others.

An important aspect when using a MIP as a selective receptor in chemical sensing is the selection of the appropriate transducer for transforming the corresponding MIP binding event into an analytical signal. Different methods for the integration of MIPs with the transducer have been reported in the literature [15] and have been applied to the fabrication of electrochemical sensors [16,17]. MIPs have been prepared *in situ* by electropolymerization in the presence of the template [18,19]. This is an easy and fast technique producing stable membranes with controlled thickness and good adherence to the electrode surface. However, these sensors often show poor selectivity. Drop-casting, spin-coating or spray coating of a pre-polymerization mixture onto the transducer surface [20] are other easy and rapid reported methods. The resulting membranes have proved to be stable in both aqueous and organic solutions. All these techniques are limited to particular polymer formulations and often involve laborious synthesis processes.

Entrapping the MIP particles into gels [21] or using different types of composites such as inks containing conductive carbon materials [22] or composites containing MIP particles, graphite and a solid binding matrix [23] are alternative methods for the fabrication of MIP-based electrochemical sensors. These types of membranes are susceptible to non-specific adsorption, leakage and the preparation procedure is also laborious. The advantage of this approach is the possibility to use established MIP formulations.

Another approach for the preparation of MIP-based sensors combines the methods explained above and consists of the electrosynthesis of a polymeric matrix for the entrapment of the MIP particles onto the transducer surface [15,18]. With this approach, a conducting polymer is synthesized electrochemically in the required monomer solution also containing the MIP suspension. Thus, MIP microparticles are entrapped within the generated polymer matrix and in turn directly immobilized onto the transducers surface. One of the most appealing aspects of this approach is the possibility of decoupling MIP synthesis and immobilization, thus enabling better optimization of each step separately. At the same time it takes advantage of the versatility of the electrochemical polymerization processes that enables a strict control over the membrane thickness and the surface active area of the synthesized polymer layer.

Diphenylamine (DPA) is an agrochemical product with high antioxidant properties widely employed to control storage scald on apples and pears [24]. Considering its low solubility in water, it is not completely removed from the fruit and therefore, DPA and its derivatives can appear in processed products such as apple juice. This product is included in the third European Union (EU) list of priority pollutants [25] and actually its use is no longer authorized within the EU [26]. Therefore, as a reference the maximum allowed concentration for apples and pears established in the EU directive 91/414/EEC was between 5 and 10 mg kg⁻¹. The analytical techniques for the determination of diphenylamine are based on gas chromatography, high-performance liquid chromatographic combined with different detection techniques, mass spectrometric methods and spectrophotometry. Although these methods are quite sensitive, they require treatment of the sample, are usually time consuming and use expensive instrumentation. Regarding sensors for DPA detection, no any electrochemical sensor has been reported in the literature.

In the present work, the fabrication and characterization of a miniaturized thin-film voltammetric sensor for the detection of DPA is presented. MIP particles were synthesized following

a protocol previously described [27] and deposited on the surface of microfabricated gold electrodes [28] by entrapment in an electropolymerised poly(3,4-ethylenedioxythiophene) (PEDOT) membrane. The use of miniaturized thin-film electrodes has multiple advantages for the preparation of MIP based sensors. Firstly, the miniaturized size of these sensors permits the use of small amounts of all the required reagents and solutions and secondly, the use of deposition techniques scalable to mass production is feasible. MIP based sensors have been optimized according to the electropolymerization time and have been characterized for DPA detection. The good results obtained with this sensor have permitted to test their feasibility for DPA measurements in spiked apple juice samples.

2. Materials and methods

2.1. Reagents and solutions

Acetonitrile (99%), magnesium perchlorate hydrate (99%), 3,4-ethylenedioxythiophene (97%), 1-naphthylamine (98%), nitric acid (69%), methanol (99%), potassium nitrate (99%), potassium hydroxide (85%), potassium ferricyanide (99%), catechol, bisphenol A and gallic acid were all purchased from Sigma–Aldrich and used as received. Acetic acid glacial (99.7%) was purchased from Panreac and used as received. All solutions were prepared using de-ionized water.

Real samples of concentrated apple juice were purchased from supermarket.

2.2. Apparatus

Gold thin-film electrodes were fabricated at the Instituto de Microelectrónica de Barcelona (IMB-CNM) according to standard photolithographic technology. The fabrication process is explained elsewhere [29]. Working area of the electrode was 4.39 mm². Three-electrode amperometric cell was used for batch measurements, which included a gold electrode as working electrode, an external Pt counter electrode (XE100, Radiometer Analytical, Villeurbanne CEDEX, Lyon, France) and a Ag/AgCl (KCl 10%, w/v) reference electrode (0726.100 Metrohm, Herisau, Switzerland). A μ -Autolab potentiostat/galvanostat (EcoChemie B.V., Utrecht, The Netherlands), using GPES 4.7 software package (General Purpose Electrochemical System) was used for batch voltammetric measurements.

SEM images were recorded on the gold coated polymeric films using a scanning electron microscope (SEM, Auriga from Zeiss) operated at 5–10 kV.

2.3. Electrode preparation

Polymers imprinted with DPA were prepared according to the procedure reported elsewhere [27]. Briefly, methacrylic acid (MAA) was used as a monomer, trimethylolpropane trimethacrylate (TRIM) as a cross-linker, 2,2'-azobis(2-methylpropionitrile) as a catalyst and acetonitrile as a solvent. Synthesis was run under nitrogen atmosphere at 60 °C. Imprinted polymers were prepared using monomer/template ratio 7.5 and polymerization time 10 h. The respective non-imprinted polymer (NIP) was selected for the electrode membrane preparation according to the previous results [27].

Prior to the membrane deposition, gold electrodes were chemically cleaned and electrochemically activated. First, the electrode surface was rinsed using a brush successively wetted in ethanol, deionized water, sulphuric acid (6M) and deionized water, and then dried under nitrogen flow. Electrochemical activation was

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