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SENSING OF FURFURAL BY MOLECULARLY IMPRINTED POLYMERS WITH ELECTROCHEMICAL TRANSDUCTION

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The determination of furanic compounds at different concentration levels in an aqueous medium, as for example beverages, is becoming a crucial task in food control, because of the relevance of these substances for food flavor and also for their possible toxic and carcinogenic effects on the human beings. For these reasons, their determination by fast, easy and low-cost methods is of interest. In the present investigation, the possibility of using molecularly imprinted polymer (MIP)-modified electrochemical sensors for the detection of a particular furanic derivative, furfural (2-furaldehyde (2-FAL)), in aqueous media is examined. Chemical sensors are based on the strict integration of a receptor with an instrument able to generate a signal upon the combination of the receptor with the substrate. Both the characteristics of the binding reaction, in particular the affinity constant, and that of the transducer, for example the sensitivity, are of overwhelming relevance for determining the performance of a sensor.

In the present work, we examine a solid synthetical receptor (MIP) obtained by non-covalent molecular imprinting of 2-FAL connected with an electrochemical transduction method. MIPs have been widely demonstrated to be advantageous with respect to the biological receptors, in particular in the field of sensing, in terms of reproducibility, fast and low cost development, stability in time and possibility of application in non physiological conditions [1, 2]. A drawback consists in the heterogeneity of the binding sites, particularly when the MIPs are synthesized by non covalent bulk procedure [2], which on the other hand could allow to perform measurements at different concentration levels. The detectable concentration level, in turn, depends on the sensitivity of the detection technique employed. Various MIP electrochemical sensors have been developed in the last years [3,4] for the determination of a number of small molecules. The voltammetric sensor here proposed is particularly convenient because of the low cost, good reproducibility and easy preparation [4]. It is composed of a screen printed cell (SPC) with graphite ink working and auxiliary electrode, and silver ink quasi-reference electrode, obtained by the screen printing technique, and of a MIP layer deposited over the whole cell. The signal is generated by the substrate itself, i.e. 2-FAL, since it is electroactive [5]. The signal is the peak current (i_p) obtained by square wave voltammetry (SWV), which is directly proportional to the analyte concentration in the polymeric layer near the working electrode. This in turn depends on the concentration in the solution phase, the binding to the MIPs taking place according to the Langmuir adsorption isotherm [2]. A typical voltammogram is reported in Figure 1b. The sensitivity of the SWV electrochemical detection depends on the experimental condition, for example the acidity of the solution, and on the SWV conditions. These have been optimized

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by the Experimental design (ED) method, in order to have a maximum peak current, and at the same time a minimum background current.

The sensitivity was improved about 10 times by changing the SWV conditions from $E_{step}=0,01$ V, $E_{pulse}=0,025$ V, $f=25$, to $E_{step}=0,03$ V, $E_{pulse}=0,065$ V, $f=28$ s⁻¹, allowing to lower the detection limit of a factor of ten.

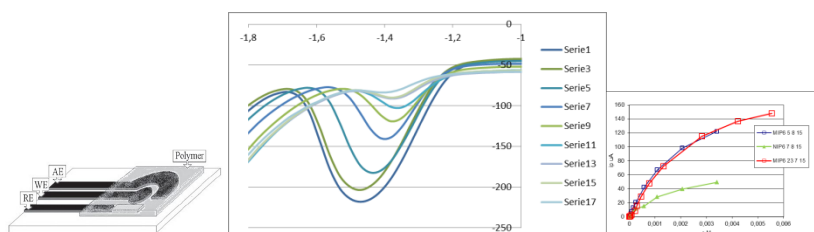


Figure 1. a) Schematic view of SPC modified with MIP. b) SWV voltammograms of 2-FAL in NaCl 0.1 M at MIP-modified sensor at $E_{step}=0,03$ V, $E_{pulse}=0,065$ V, $f=28$ s⁻¹. Concentration of 2-FAL from $2 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ M. c) Binding isotherms of MIP and NIP modified sensor in water at pH=6 NaCl 0.1 M.

At optimized conditions the electrochemical sensor shows an LOD of about $6 \cdot 10^{-6}$ M for 2-FAL at neutral pH in an aqueous 0.1 M NaCl solution and in a white wine real sample.

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