

A molecularly structured receptor (MIP) for a chemosensor for furfural with electrochemical transduction

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The application of a molecularly imprinted polymer (MIP) [1] as a receptor for electrochemical sensing is demonstrated in the case of the determination of 2-furaldehyde (furfural, 2-FAL) in aqueous matrices. Furfural is a molecule largely diffused, since it naturally derives from the acid-catalyzed degradation of xylose in lignocellulosic biomass. Moreover, it is produced in food by sugar dehydration and by the Maillard reaction, and can determine the organoleptic properties of food. It is also of interest in the production of biofuels, and can provide a large quantity of useful derivatives, representing a sustainable, abundant and cheap source of different chemicals. For these reasons, the determination of furfural in different matrices is of high interest. Various methods have been proposed for the determination of furfural, much of them based on chromatographic techniques. They are generally quite demanding in terms of time and complexity of chemical operations and instrumentation.

Sensors appear to be the best solution for analytical determinations in a short time, and possibly in situ, since such devices are able to reduce handling operations and dimensions of the analytical apparatus.

Electrochemical transduction based on voltammetry can be considered as an ideal approach for the determination of electroactive substances [2], however it is not very selective.

The use of a molecularly structured medium in the electrochemical cell should improve this aspect, ensuring a better selectivity as previously shown in the case of a different substance [3]. MIPs are obtained by polymerization of a liquid mixture containing aggregates of the analyte of interest (furfural in the case here considered) with a polymerizable molecule. In the case here considered, the polymeric mixture consisted of the analyte (furfural), a functional monomer (MAA), and a crosslinker (EGDMA) at molecular ratio

1:4:40, and of a radical initiator (AIBN), sometimes with a porogen solvent. For the sake of miniaturization, the electrochemical cell consists in a commercial screen-printed cell (SPC) composed of a graphite ink-working electrode, a graphite ink auxiliary electrode and an Ag ink quasi-reference electrode on a polyester support. A MIP layer is formed directly over the whole cell by dropping a small amount of the prepolymeric mixture over it, and by polymerizing at high temperature (72°C) in the air. Furfural was extracted from the obtained polymeric layer by repeated washing with ethanol. For the sake of comparison, a corresponding NIP (Not Imprinted Polymer) was synthesized as well. The obtained MIP layer was microporous, with connected pores, so ensuring a good electrical conductivity of the medium in contact with the electrodes.

The affinity and the selectivity of the molecularly structured imprinted sites in the polymeric layer was determined by electrochemical measurements (cyclic voltammetry and square wave voltammetry) carried out in the MIP modified cell described, and compared with the same characteristics determined by batch adsorption procedure. Affinity constants as high as 10^6 - 10^7 M⁻¹ could be obtained, with good selectivity even for compounds of similar structure, as other furanic derivatives.

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