

Molecularly imprinted polymer as molecularly structured receptor for chemosensors based on SPR and SWS on plastic optical fiber for industrial application

Simone Marchetti¹, Maria Pesavento¹, Nunzio Cennamo², Luigi Zeni²

¹ Department of Chemistry - University of Pavia, Pavia, 27100 Italy

² Department of Industrial and Information Engineering - University of Campania, Aversa (CE), 81031 Italy

simone.marchetti01@universitadipavia.it

The development of new sensory methods, based on synthetic biomimetic receptors i.e. Molecularly Imprinted Polymers (MIP), suitable for the specific detection of different analytes in a real or native matrix, like biological or environmental samples and matrices of industrial interest, with an enhancement in the limit of detection and selectivity, is highly required [1]. The molecularly imprinted structure of the synthetic receptors (MIP) is crucial for obtaining good affinity and selectivity of the interaction sites. Specific cavities must be designed for the detection of the analyte molecule in the desired complex matrix. For this reason, identification of appropriate functional monomers was performed to optimize the MIP characteristics and obtain a proper receptor. To this aim, a computational method (Gaussian 09), has been employed in the present work to develop a MIP for dibenzyl disulphide (DBDS), an antioxidant of industrial interest. Non-covalent interactions (such as electrostatic or hydrogen bond) are considered to meet the prerequisites of an easy and rapid re-utilization of the sensor. The functional monomers interacts with the analytes molecule, which act as template, and create a pre-assembly. Then, by adding a cross-linking agent and an initiator, polymerization takes place around the pre-assembled molecule cluster mold and the 3D structure of the site is fixed. At the end of polymerization process, the template is removed by washing, so that sites with complementary shape are exposed.[2] An important point in the preparation of these nanostructured solid receptors is their physical form which must be constructed considering the sensing transduction method. In the present research MIPs were used as receptors in two kinds of optical platforms both relying on plastic optical fibers (POFs). One was

based on surface plasmon resonance (SPR) [2] and the other on segmented waveguide (SWS) [3] platforms. In the first case the sensing is based on surface plasmon resonance (SPR) phenomena taking place at the interface MIP-thin gold layer. A shift in resonance wavelength is produced by the variation of the refractive index of the polymer when the analyte rebinds [2]. The segmented waveguide platform, SWS, is based on two plastic optical fibers coupled through a trench, filled with the MIP [3]. The relative output, i.e. the ratio of the light intensity from the two fibers (I_1 / I_2) decreases when the DBDS concentration increases. The instrumentation required is similar to that of SPR method but could be even simpler and cheaper. In both kinds of platforms MIP was polymerized directly on the platform. LOD of SWS platform of $6,25 \times 10^{-7}$ M is compared with that of SPR of $1,47 \times 10^{-8}$ M for DBDS in power transformer oil. The SWS platform has higher LOD than SPR platform, but it is more reproducible due to the simplicity of its fabrication.

References

- [1] L. Uzun, A. P.F. Turner, *Bios.Bioel.*, **2016**, 76, 131-144
- [2] N. Cennamo, L. De Maria, G. D'Agostino, L. Zeni, M. Pesavento *Sensors*, **2015**, 15, 8499-8511
- [3] N. Cennamo, G. Testa, S. Marchetti, L. De Maria, R. Bernini, L. Zeni, M. Pesavento, *Sens and Act B* **2017**, 241, 534-540