Validation of sensors based on nanostructured catalytic biomimetic polymers with tyrosinase activity for phenols detection in natural and waste waters.

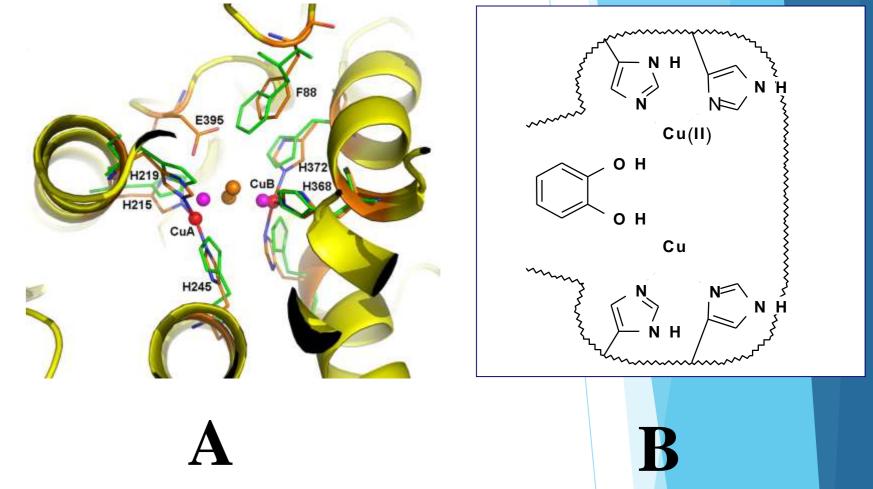
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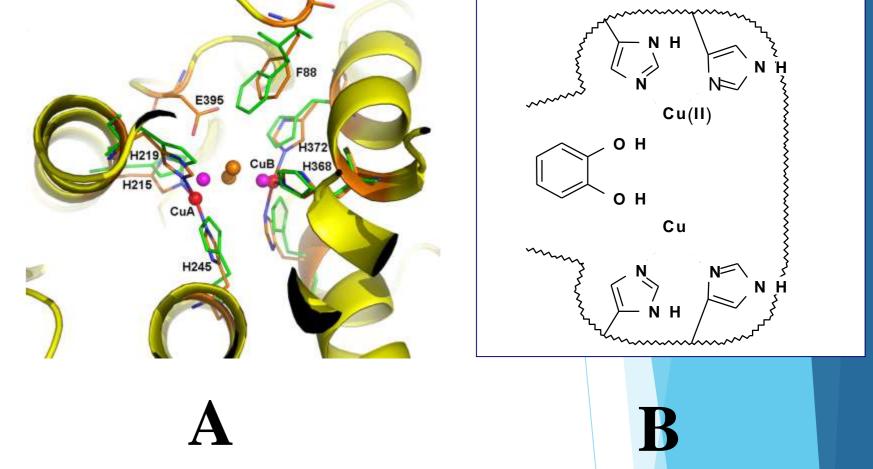
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Abstract





Nanostructured polymers with tyrosinase activity capable of selective cleavage of *o*-hydroxyphenols were synthesized using the method of molecular imprinting. The catalytic molecularly imprinted polymers (MIP) were obtained by co-polymerization of 4imidazolacrylic acid, ethyleneglycoldimethacrylate, and Cu(II) in the presence of *o*-hydroxyphenol as a template molecule (Fig. 1,b). The synthesized nanostructured polymers were used as a sensitive part of the biomimetic sensor based on a portable oxygen-meter for *o*-hydroxyphenol revealing in aqueous samples. The sensor provided detection of o-hydroxyphenols within the range 0.08–2.5 mM with the detection limit 0.08 mM (Fig. 2). The selectivity of the developed sensors as for the detection of different phenols was investigated using o-hydroxyphenol, phenol, 2-nitrophenol, 4nitrophenol, o-cresol, p-cresol, 2-methoxyphenol, m-hydroxyphenol, 2-(3,4)-dihydroxyphenyl)-ethylamine, and1,2,3-trihydroxybenzene analytes (Fig. 3). High selectivity of the synthesized as nanostructured polymers with tyrosinase activity towards ohydroxyphenols was confirmed. Methods of calibration of the laboratory prototypes of the sensor device based on biomimetic polymers for the determination of *o*-hydroxyphenols in natural and wastewaters were developed. The analysis of real samples of natural and wastewaters from Kyiv, Cherkasy, Odesa, and Sumy regions of Ukraine as for the content of o-hydroxyphenols was carried out using the developed sensor systems. A comparison of the biosensor analysis data with the results of traditional analytical methods was made and good correlation between the data obtained with different methods was demonstrated. The proposed method is superior to traditional analytical methods in terms of the simplicity of the analytical procedure, its cost, as well as the cost and compactness of the equipment.

Fig.1. Possible structure of mamalian tyrosinase active site according to García-Borrón J.C. and Solano F., 2002 (A) and possible structure of the MIP with tyrosinase activity (B)

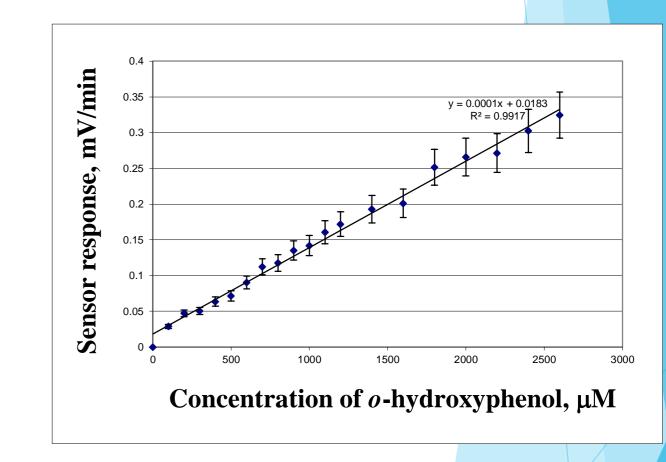


Fig.2. Typical calibration graph of the catalytic MIP-based sensor for *o*-hydroxyphenol detection in aqueous samples

Acknowledgement

Financial support from National Academy of Sciences of Ukraine is gratefully acknowledged.

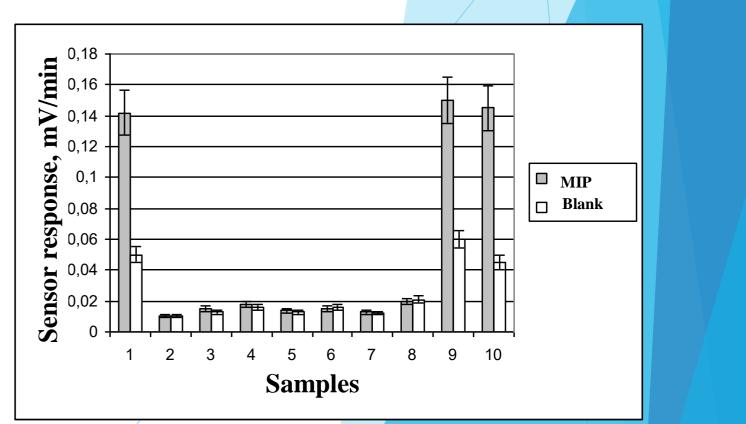


Fig.3. Responses of the *o*-hydroxyphenol-selective sensor in response to addition of 1 mM of *o*-hydroxyphenol (1), phenol (2), 2-nitrophenol (3), 4-nitrophenol (4), o-cresol (5), *p*-cresol (6), 2-methoxyphenol (7), *m*-hydroxyphenol (8), 2-(3,4)-dihydroxyphenyl)-ethylamine (9), and 1, 2, 3trihydroxybenzene (10) as analytes