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REVIEW

Ph.D. Thesis

„Molecularly imprinted polymers-based chemosensors for selective determination of chosen food toxins"

Author: Viknasvarri Ayerdurai

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Ph.D. Thesis of Viknasvarri Ayerdurai concerns very vivid research area.
The application of molecularly imprinted polymers in the sensor's development becomes more and more popular. This approach has numerous advantages over other sensing technology.
The most important is avoiding the necessity of using the very sensitive biological materials as a sensing element.
The incorporation of the „shape" of molecules responsible for selective target recognitions into appropriate polymer matrix belongs to the very smart technology.

Mrs. Viknasvarri Ayerdurai has undertaken research concerning the development of electrochemical sensors based on molecularly imprinted polymers destined for selective determination of **tyramine**, which may cause the hypertensive crisis and 2-amino-3,7,8 – trimethyl-3*H*-imidazo[4,5-*f*]quinoxaline (**7,8-DiMeIQx**), considered as a potent hazardous carcinogen.

Ph.D. thesis of Viknasvarri Ayerdurai was edited very carefully. The „Literature Review" Chapter, divided into four sub-chapters, contains the crucial information about the fabrication methods of molecularly imprinted polymers (MIPs), electrochemical techniques as well as food toxins being the objectives of the thesis. This chapter is saturated with the relevant literature, since the article published by Pauling in 1940, till numerous articles published in 2021. There is no doubt, that this chapter could be a valuable guide for the young researchers intending to be involved in this research area.

The Chapter 2 „Experimental" was prepared very well. The Table with structures and names of compounds used for the study is very informative.

The fundamentals of techniques used for the research: cyclic voltammetry (CV), differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS), Atomic force microscopy (AFM), Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy have been described in a strict manner proving of Mrs. Viknasvarri Ayerdurai knowledge.

In chapter describing the fabrication procedures of molecularly imprinted polymers (MIPs), Mrs. Viknasvarri Ayerdurai has underlined the crucial step of pre-selection of functional and cross – linking monomers for a given template, which was done by: (i) chemical intuition, (ii) procedures previously reported in the literature, and (iii) availability of the functional monomers. The second step involved computational modelling of the pre-polymerization complexes in order to optimize the structures and calculate the Gibbs free energy change of formation of template and functional monomer complexes. The modelling study reduce significantly experimental work. The next steps of MIPs fabrication concerns: dissolution of components, electrochemical MIP film deposition on the electrode surface, and finally, template extraction. The non-imprinted polymer (NIP) was prepared in the same way as MIP, but in the absence of template. NIP serves as a control material and was used to determine the extent of imprinting.

Mrs. Viknasvarri Ayerdurai has been developed successfully the electrochemical sensor based on MIP for selective determination of tyramine. These results have been published in Bioelectrochemistry, 2021, 138, 107695.

The sensor prepared based on FM1 monomer was not selective. In order to get better selectivity towards tyramine, Mrs. Viknasvarri Ayerdurai applied the crown – ether – moiety – containing monomer FM2. This decision has been supported by DFT calculations.

After optimization of MIP-2 film deposition on the Pt electrode surface and template removing, the surface of sensor was carefully characterized with using numerous techniques: PM-IRRAS, XPS, AFM, SEM. The sensor based on FM2 was successfully applied for selective determination of tyramine with using DPV as well EIS methods in the presence of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ as a redox probe. The NIP-2 film coated electrode show almost no response towards tyramine. Finally, the obtained sensor was successfully applied for tyramine determination in the presence of Mozzarella cheese whey.

Detailed comments

There are mistakes in graphical abstract. In figure concerning EIS - 490 mM and 290 mM should be 490 μM and 290 μM. In Figure concerning DPV - 1,01 μM, should be 1,01 mM. These figures would be clearer, if particular tyramine concentration would be presented in the same colour (in DPV and EIS).

In Figure 3.2-3 the DPV peak current should decrease with increase of tyramine concentration.

Figure 3.2.-10 – in caption there is lack of description of curve 8".

Another sensor developed by Mrs. Viknasvarri Ayerdurai was destined for the determination of quinoxaline heterocyclic aromatic amine (**7,8-DiMeIQx**).

The results obtained was published in J. Agric. Food Chem., 2021, 69, 14689.

It is known that this carcinogen compound has ability to intercalate in a dsDNA. Thus, the monomers containing adenine (**Abt**) and thymine (**Tbt**) in order to mimic dsDNA was applied for MIP film preparation.

The calculation of Gibbs free energy change accompanying the forming of the complexes with the different molar ratio **Abt: 7,8-DiMeIQx: Tbt** allows for selection of the most stable one, suitable for MIP film preparation. The selected MIP film was deposited on the surface of Au – electrode.

DPV measurements in the presence of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ redox probe showed similar responses of MIP and control - NIP film – coated electrode after 7,8-DiMeIQx addition to the test solution. In order to avoid the lack of selectivity, the different transduction - impedimetric capacitance (CI) was applied. With using this technique selective responses towards 7,8-DiMeIQx were observed for MIP film coated electrode. NIP electrode showed no response.

Detailed comments

Figure 4.2- 4 – in caption there is lack of description of curve 5'.

I would like to know the opinion of Mrs. Viknasvarri Ayerdurai which conditions: steady state or FIA are the most suitable for practical sensor application?

The two electrodes were applied: Au and Pt. Which one is more suitable for MIPs film deposition and why?

Is it possible to estimate the number of binding sites on the surface of MIP coated electrode? This parameter would be very helpful for selection of appropriate analyte concentration range.

I do appreciate the „Summary and future prospective" chapter encouraging other young researchers to be involved in this vivid research area. There is no doubt that the reach food matrix generates the one on the biggest problem in sensors development. I would like to invite Mrs. Viknasvarri Ayerdurai to discuss this issue.

Mrs. Viknasvarri Ayerdurai is very an active young scientist. She participated in numerous conferences delivering oral presentation as well presenting posters.

During the realization of Ph.D. thesis, Mrs. Viknasvarri Ayerdurai has been very much involved in the international co-operation.

Also, I would like to underline interdisciplinary experience, which Mrs. Viknasvarri Ayerdurai has gained during the Ph.D. thesis realization.

In conclusion, I would like to ask the Scientific Council of Institute of Physical Chemistry of Polish Academy of Sciences to continue the procedure connected with Ph.D. thesis of Mrs. Viknasvarri Ayerdurai.

Best regards,

Hanna Radecka

Professor Hanna Radecka