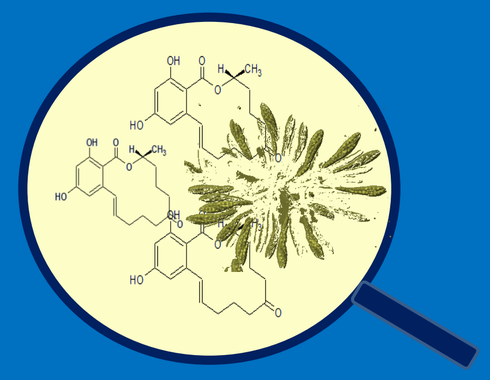
Chip based plasmon-enhanced fluorescence sensor for highly-sensitive zearalenone analysis

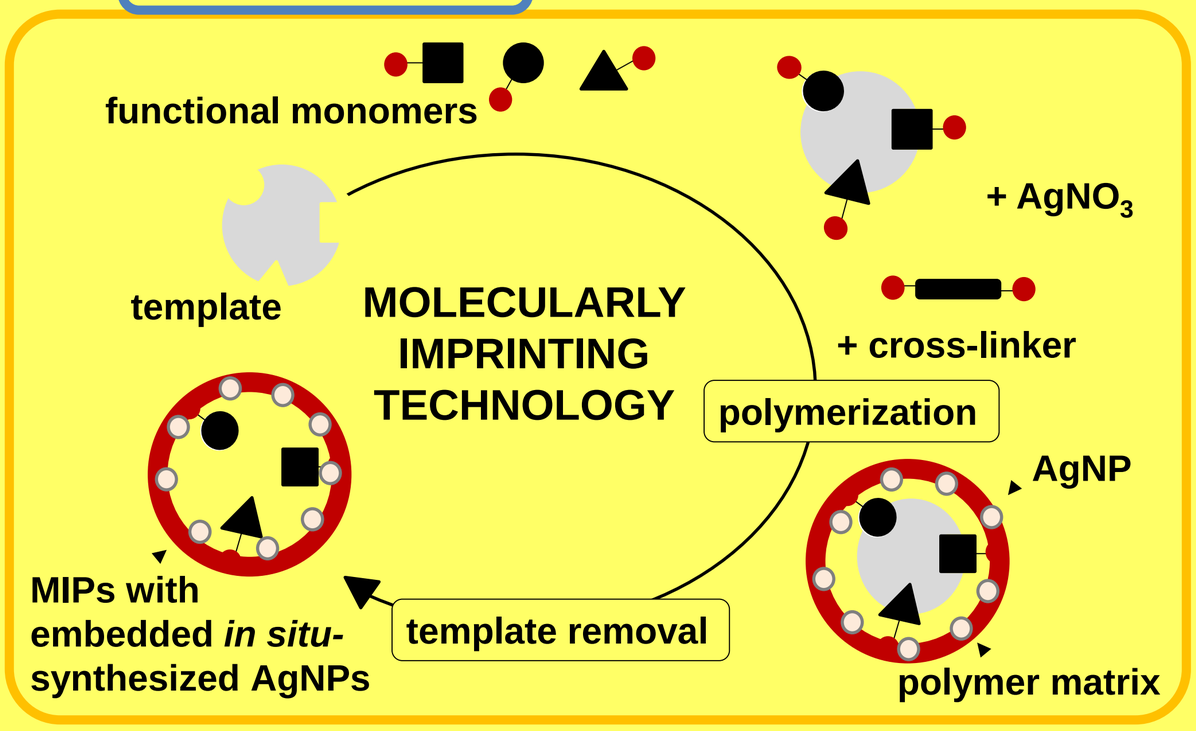


Yarynka D.V.[1], Chegel V.I.[2], Dubey I.Ya.[1], Dubey L.V.[1], Stepanenko Ye.Yu[1], Brovko O.O.[3], Sergeyeva T.A.[1]

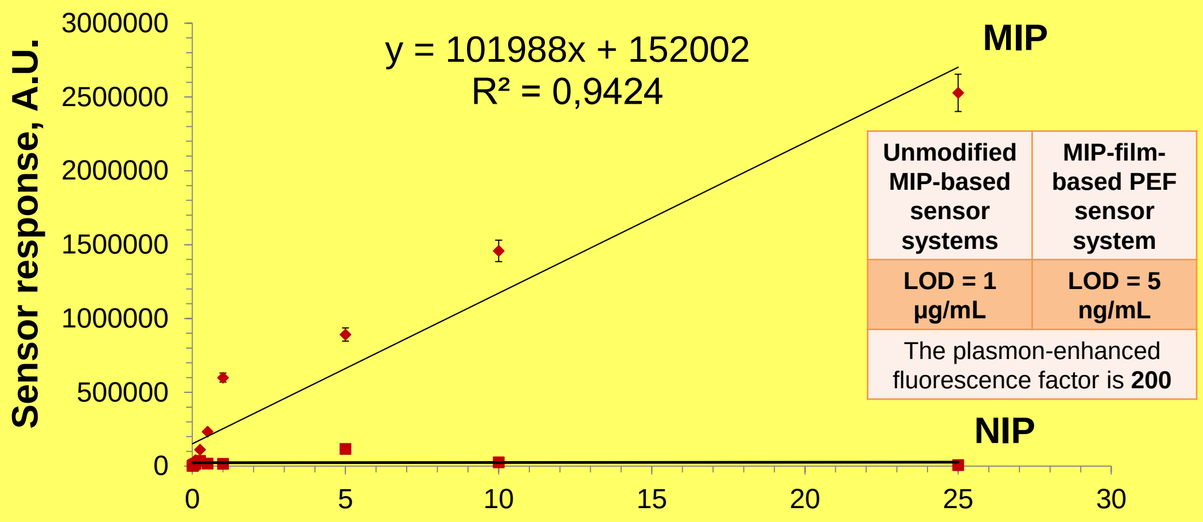
Abstract

The highly-sensitive chip-based plasmon-enhanced fluorescence (PEF) sensor system for fast and robust zearalenone analysis in grain foods was developed. Thin molecularly imprinted polymer (MIP) films with embedded *in situ*-synthesized Ag nanoparticles (AgNPs) immobilized on the surface of glass slides were used as sensing chips for the proposed PEF-based sensor system. The MIP films were synthesized according to a dummy template-based approach with cyclododecyl-2,4dihydroxybenzoate as a template molecule and ethyleneglycolmethacrylatephosphate as a functional monomer. AgNPs were *in-situ* synthesized using reduction of $AgNO_3$ which was added to the monomer composition. Spherical AgNPs (20–30 nm in diameter) were formed in MIP films structure during the pre-heating step and further UV-initiated polymerization procedure on the surface of glass slides. To provide covalent immobilization of the MIP films, glass slides were treated with γ-methacryloxypropyltrimethoxysilane. Enhanced fluorescence of ZON selectively adsorbed on the surface of glass chips coated with thin MIP films was registered with the standard laboratory spectrofluorimeter. The transmission electron microscopy was used to investigate the morphology and size of AgNPs embedded in the MIP film structure. The influence of $AgNO_3$ concentration on the PEF phenomenon was also investigated. The LOD of ZON sensor chips was 5 ng/mL, and the linear detection range was 5-25 ng/mL. The developed AgNPs-containing MIP-based PEF sensor chips were successfully used for the analysis of ZON contamination in spiked and naturally contaminated grain samples.

Results

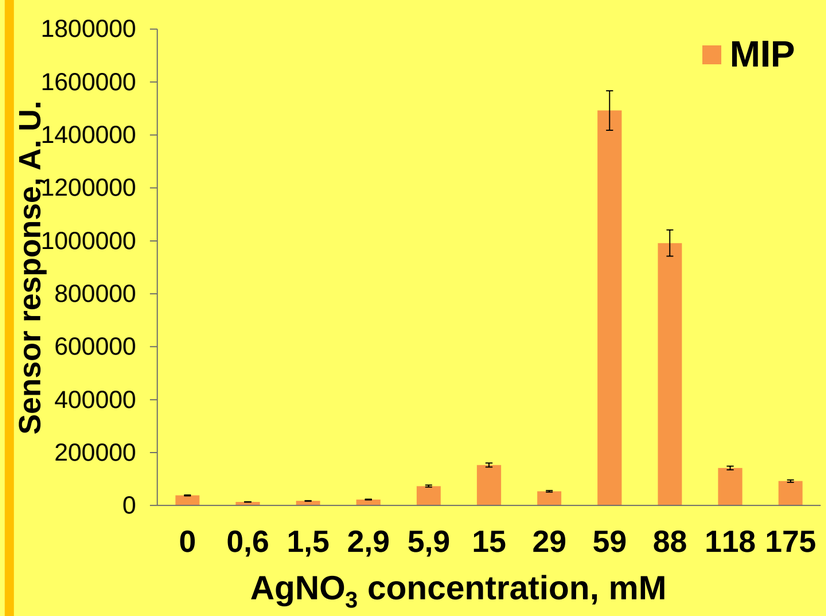


Calibration plots of the AgNPs-containing MIP-film-based PEF sensor systems for ZON detection.

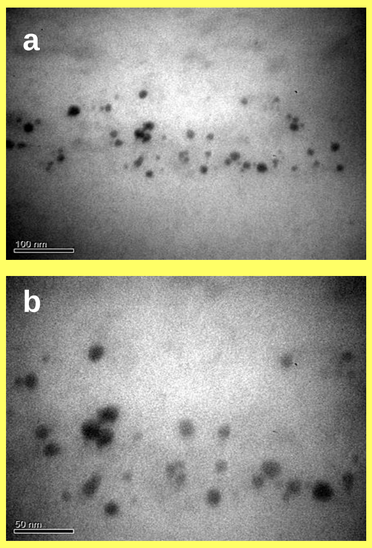


Fluorescence of AgNPs-containing MIP and NIP thin polymeric films immobilized on the glass slides synthesized with EGMP as a functional monomer with the addition of 59 mM $AgNO_3$.

The influence of $AgNO_3$ concentration on the PEF phenomenon



Fluorescent sensor responses of the sensors based on AgNPs-containing MIP thin films synthesized with different $AgNO_3$ concentrations in response to the addition of 10 µg/mL ZON.



TEM images of AgNPs formed in the structure of MIP thin polymer films taken at different magnifications (scale 100 nm (a) and 50 nm (b)). JEM-1230, JEOL, Japan.

Detection of zearalenone in real maize and wheat flour samples

No.	Sample	Amount of ZON in the sample	Amount of ZON in the sample determined
1	Quality control material Zearalenone in corn, high level (Romer Labs)	293 ± 59 µg kg^{-1}	278.3 ± 5.5 µg kg^{-1}
2	Quality control material Zearalenone in corn, low level (Romer Labs)	55 ± 15 µg kg^{-1}	53.2 ± 1.4 µg kg^{-1}
3	maize flour “Lavka Tradytsiy”, Ukraine	25 ng mL^{-1}	24.6 ± 2.8 ng mL^{-1}
5	wheat flour “Khutorok”, Zmiiv, Ukraine	50 ng mL^{-1}	50.8 ± 0.7 ng mL^{-1}

n=6 in all the experiments

Acknowledgement. Financial support from National Academy of Sciences of Ukraine (program of scientific research «"Smart" sensor devices of the new generation based on modern materials and technologies» 2018-2022) is gratefully acknowledged.

[1] *Institute of Molecular Biology and Genetics of the NAS of Ukraine. Zabolotnogo str. 150, Kyiv-03143, Ukraine. E-mail: d.v.yarinka@imbg.org.ua*
[2] *V.E. Lashkaryov Institute of Semiconductor Physics of the NAS of Ukraine, Prospect Nauky, 41, Kyiv- 03680, Ukraine.*
[3] *Institute of Macromolecular Chemistry of the NAS of Ukraine. Kharkivske Shosse, 48, Kyiv-02160, Ukraine.*