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Single Drop Detection of Furfural in Wine by An SPR-optical Fiber-MIP Based Sensor †

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Abstract: A surface plasmon resonance (SPR) platform, based on a D-shaped plastic optical fiber (POF), combined with a biomimetic receptor, i.e. a molecularly imprinted polymer (MIP), is proposed to detect 2-furaldheide (2-FAL) in fermented beverages as for example wine. The determination of 2-FAL in food samples, is becoming a very crucial task on the one hand for its role on the flavor and on the other in relation to its toxic and carcinogenic effect on the human beings. The proposed sensing device is easy to use and cheap, and has been tested successfully for the detection and quantification of substances of interest in different fields, as health, environment and industry. The possibility of performing single drop measurements is a further favorable aspect for practical applications. As an example, the use of an SPR-MIP sensor for the analysis of 2-FAL in wine, in a concentration range useful for practical applications, is here described.

Keywords: molecularly imprinted polymer (MIP); surface plasmon resonance (SPR); plastic optical fiber (POF); 2-furaldheide (2-FAL); wine.

1. Introduction

Biosensors and chemical sensors in optical fibers have been shown to be able to play an important role in numerous application fields [1-5], in particular the devices based on the SPR phenomenon have shown promising merits of low-cost, high sensitivity, and small-size [6-11].

The Kretschmann and Otto configurations are widely used in practice, but these sensor systems usually require bulky and expensive optical equipment. Incorporating optical fiber makes it possible to reduce the cost and dimensions of the SPR sensors, with the possibility to integrate the sensing platform with small optoelectronic devices (sources and detectors). For low-cost sensing systems, POFs are especially advantageous due to their excellent flexibility, easy manipulation, great numerical aperture, large diameter, and the fact that plastic is able to withstand smaller bend radii than glass.

The optical sensor system here proposed has been developed by our research group [12-19] and is based on a multilayer structure realized on a planar surface of exposed core POF, embedded in a resin block (D-shaped POF platform), with the MIP receptor for 2-FAL detection deposited on the gold film.

This optical sensing platform has been exploited in several applications, employing different kinds of receptors, as antibodies, aptamers, molecularly imprinted polymers (MIPs), and also metal ligands, as for example hydroxamate siderophore deferoxamine for iron(III) and D,L-penicillamine for copper(II) detection [12-19].

The aim of this work is to test the possibility of using the SPR-MIP sensor (i.e. exploiting an MIP receptor specific for 2-FAL combined with an SPR-POF platform) for determining the concentration of 2-FAL in water solutions for food safety controls. Wine has been considered an interesting matrix since the 2-FAL detection in wine is becoming a very crucial task not only for its relevance in affecting the flavor and aroma [20], but also for its toxic and carcinogenic effect on the human beings.

2. Methods

The preparation of the SPR-POF optical platform has been widely described [12, 14, 17]. It is based on a multimode POF (0.96 mm diameter) embedded at a surface of a resin holder (1x1 cm). It presents a characteristic D-shaped sensing region obtained by erasing the cladding and partially the core of the POF, with a polishing process. A multilayer structure is built up over the exposed POF core, with a buffer layer (a photoresist of high refractive index, 1.5 μm thick), a thin metal film (gold, 60 nm thick) and, finally, an MIP layer as a specific chemical receptor for 2-FAL detection. The sensing region is 1 cm long. The flat shape makes it possible to perform the measurement in a drop deposited over the flat sensing region. As reported in Figure 1, the measurement apparatus consists of a halogen lamp (HL–2000–LL, Ocean Optics) illuminating the sensor and a spectrometer connected to a PC (USB2000+UV–VIS spectrometer, Ocean Optics) [12,13].

The MIP was prepared in situ, dropping over the gold layer a small volume of the MIP prepolymeric mixture, spinning and polymerizing in an oven. The prepolymeric mixture, prepared according to the procedure reported in [17], was composed of the reagents at molar ratio 1 (2-FAL):4 (MAA):40 (DVB) as reported in [17]. Divinylbenzene (DVB), the cross-linker, was also the solvent in which the functional monomer (that is, methacrylic acid, MAA), and the template, 2-FAL, are dispersed. DVB is at the same time the cross linker and the solvent, being a liquid present in large excess. The mixture was uniformly dispersed by sonication and de-aerated with nitrogen for 10 min. Then the radical initiator AIBN (16 mg for 700 μl of DVB) was added to the mixture. About 50 μL of the MIP prepolymeric mixture were dropped on the SPR sensing region and spun for 2 min at 1000 rpm. Then the thermal polymerization was carried out for 16 h at 80 °C. Finally, the template was removed by repeated washings with 96% ethanol. Figure 1 shows the optical-chemical sensor system.

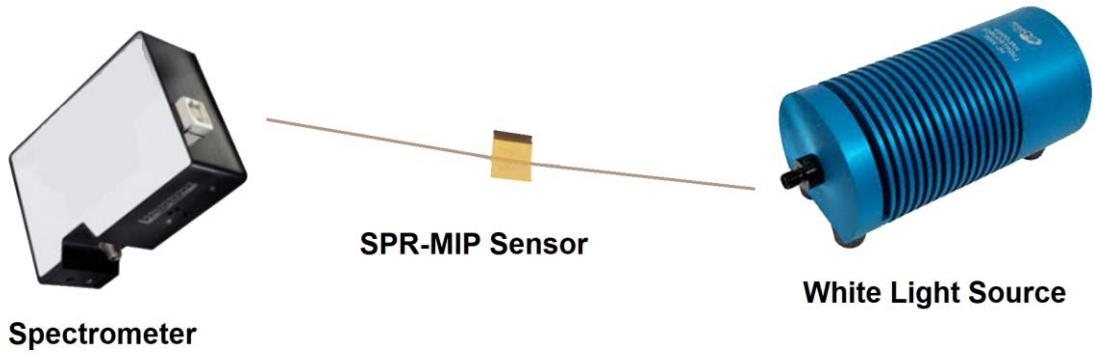

Figure 1. SPR-MIP sensor with the experimental setup.

To perform the measurements, the platform was fixed in a mini holder which was purposely designed to keep the sensing surface in a flat. A drop of sample (50 μl) was deposited over the flat part of the sensor and allowed to equilibrate for 5 minutes. During the equilibration the drop over

the surface maintains its shape, due to the hydrophobic nature of the MIP since the polymer is mainly constituted by DVB. This makes the measurement in a drop possible.

The variation of the resonance wavelength with respect to the resonance wavelength of the blank solution, not containing 2-FAL, was the recorded analytical parameter.

The sample used for the characterization was an artificial wine with a refractive index near to that of natural white wines (1.339-1.346), and not containing furanic aldehydes.

3. Results and discussion

The standardization curves were obtained by plotting the variation of the resonance wavelength ($\triangle\lambda$) in function of the concentration of 2-FAL. The curves were modelled by an equation similar to the Hill equation, deriving from the Langmuir adsorption isotherm [19]:

$$\triangle\lambda = \frac{k\ g\ c_{int} K_{aff}[A]}{1+K_{aff}[A]} = \frac{\triangle\lambda_{max} K_{aff}[A]}{1+K_{aff}[A]} \qquad (1)$$

K_{aff} is the affinity constant of 2-FAL for the MIP, c_{int} is the concentration of the specific sites obtained by the molecular imprinting, g is the mass of polymer. $\triangle\lambda_{max}=k\ g\ c_{int}$ is the maximum resonance wavelength shift ($\triangle\lambda$) obtained at high concentration of analyte. The concentration of the analyte in the sample [A] is equal to the total concentration (c_A), i.e. the concentration of the analyte adsorbed is negligible with respect to the total concentration, [A]=c_A.

The evaluation of the parameters of the standardization equation is made by the software Solver present in Excel. Once these parameters are known, the concentration of the analyte giving $\triangle\lambda$ as signal can be evaluated in the whole detection range.

The RI of the dielectric layer over gold depends on the amount of 2-FAL in the MIP layer and so on the concentration in the solution. Thus the resonance wavelength variation ($\triangle\lambda$) in function of the analyte concentration is exploited for analytical purposes. In the case of water as the sample matrix, when the 2-FAL concentration increases, the SPR wavelength is shifted to higher values as reported in Figure 2. The wavelength variation versus the analyte concentration is well fitted by eq. 1, as expected when the sorption takes place according to the Langmuir model, with a constant response ($\triangle\lambda_{max}$) for concentrations higher than 1 mg/L, corresponding to the saturation of the receptor. The parameters, evaluated by the non linear regression method, are: affinity constant, K_{aff}, 9.4 L/mg ($9.0\ 10^5$ M^{-1}), $\triangle\lambda_{max}$ = 3.3 nm, sensitivity at low concentration 31.6 nm/(mg/L). The LOD in water was 0.03 mg/L.

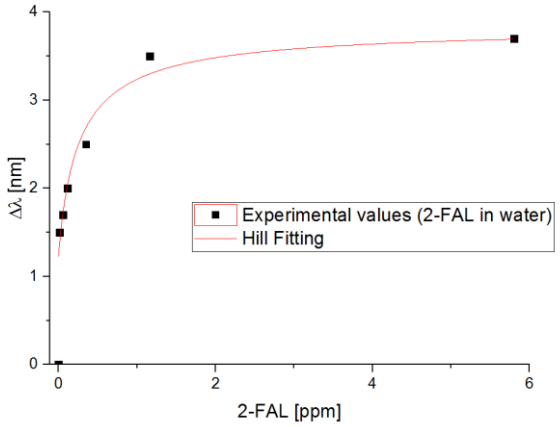

Figure 2. SPR wavelength shift versus concentration of 2-FAL in water solution with the Hill fitting to the experimental data.

In the considered artificial wine the resonance wavelength is shifted to higher values with respect to that in water. This effect could be due in part to the different refractive index of the wine, but probably mainly to the different acidity and composition, in particular to the presence of alcohol, sugars and organic acids. The dose-response curve obtained in artificial wine gave the following parameters: K_{aff}=75.6 L/mg (7.2 10^6 M^{-1}), $\triangle\lambda_{max}$=3.3 nm, sensitivity at low concentration 254.9 nm/(mg/L), LOD=0.004 mg/L.

4. Conclusions

It has been found that the "wine" matrix has a large effect on the SPR signal. In this matrix, λ_{ris} is red-shifted with respect to that in water. The response of the SPR-MIP sensor to 2-FAL is different in water and in the artificial wine, with a better sensitivity and lower detection limit in artificial wine. The affinity constant is very high both in water and in artificial wine, but it is one magnitude order higher in wine than in water. Mainly for this reason the LOD is lower in this matrix, with a detection range which is suitable for the determination of 2-FAL in wine.

This can have a high practical interest on one hand for the possible toxic and carcinogenic effects of furanic aldehydes, and in particular of 2-FAL, on human beings and, on the other hand, for their impact on the aroma.

References

1. Wang, X.D.; Wolfbeis, O.S. Fiber-Optic Chemical Sensors and Biosensors (2013-2015). *Anal. Chem*. **2016**, 203-227.
2. Leung, A.; Shankar, P.M.; Mutharasan, R. A review of fiber-optic biosensors. *Sens Actuators B Chem.* **2007**, 125, 688–703.
3. Trouillet, A.; Ronot-Trioli, C.; Veillas, C.; Gagnaire, H. Chemical sensing by surface plasmon resonance in a multimode optical fibre. *Pure and Applied Optics* **1996**, 5, 227.
4. Wang, X.D.; Wolfbeis, O. S. Fiber-Optic Chemical Sensors and Biosensors (2008-2012). *Anal Chem*. **2013**, 85**,** 487.
5. Monk, D. J.; Walt, D. R. Optical fiber-based biosensors. *Analytical and Bioanalytical Chemistry* **2004**, 379, 931-945.

6. Anuj, K.; Sharma, R. J.; Gupta, B. D. Fiber-optic sensors based on surface Plasmon resonance: a comprehensive review. *IEEE Sens J.* **2007**, 7, 1118.
7. Gupta, B.D.; Verma, R.K. Surface plasmon resonance-based fiber optic sensors: Principle, probe designs, and some applications. *J. of Sensors* **2009**, 2009, 1-12.
8. Trouillet, A.; Ronot-Trioli, C.; Veillas, C.; Gagnaire, H. Chemical sensing by surface plasmon resonance in a multimode optical fibre. *Pure and Applied Optics* **1996**, 5, 227.
9. Piliarik, M.; Homola, J.; Manikova, Z.; Čtyroký, J. Surface Plasmon Resonance Sensor Based on a Single-Mode Polarization-Maintaining Optical Fiber. *Sens. Actuat. B Chem* **2003**, 90, 236-242.
10. Jorgenson, R.C.; Yee, S.S. A fiber-optic chemical sensor based on surface plasmon resonance. *Sens. Actuators B: Chem.* **1993**, 12, 213–220.
11. Homola, J. Present and future of surface plasmon resonance biosensors. *Anal. Bioanal. Chem.* **2003**, 377, 528–539.
12. Cennamo, N.; D'Agostino, G.; Galatus, R.; Bibbò, L.; Pesavento, M.; Zeni, L. Sensors based on surface plasmon resonance in a plastic optical fiber for the detection of trinitrotoluene. *Sensors and Actuators B* **2013**, 188, 221-226.
13. Cennamo, N.; Varriale, A.; Pennacchio, A.; Staiano, M.; Massarotti, D.; Zeni, L.; D'Auria, S. An innovative plastic optical fiber-based biosensor for new bio/applications. The Case of Celiac Disease. *Sensors and Actuators B* **2013**, 176, 1008–1014.
14. Cennamo, N.; D'Agostino, G.; Pesavento, M.; Zeni, L. High selectivity and sensitivity sensor based on MIP and SPR in tapered plastic optical fibers for the detection of L-nicotine. *Sensors and Actuators B* **2014**, 191, 529-536.
15. Cennamo, N.; Di Giovanni, S.; Varriale, A.; Staiano, M.; Di Pietrantonio, F.; Notargiacomo, A.; Zeni, L.; D'Auria, S. Easy to use plastic optical fiber-based biosensor for detection of butanal. *PLOS ONE* **2015**, 10(3).
16. Cennamo, N.; Pesavento, M.; Lunelli, L.; Vanzetti, L.; Pederzolli, C.; Zeni, L.; Pasquardini, L. An easy way to realize SPR aptasensor: A multimode plastic optical fiber platform for cancer biomarkers detection. *Talanta* **2015**, 140, 88-95.
17. Cennamo, N.; De Maria, L.; Chemelli, C.; Profumo, A.; Zeni, L.; Pesavento, M. Markers detection in transformer oil by plasmonic chemical sensor system based on POF and MIPs. *IEEE Sensors Journal* **2016**, 16, 7663-7670.
18. Cennamo, N.; Alberti, G.; Pesavento, M.; D'Agostino, G.; Quattrini, F.; Biesuz, R.; Zeni, L. A Simple Small Size and Low Cost Sensor Based on Surface Plasmon Resonance for Selective Detection of Fe(III). *Sensors* **2014**, 14, 4657-4661.
19. Pesavento, M.; Profumo, A.; Merli, D.; Cucca, L.; Zeni, L.; Cennamo, N. An Optical Fiber Chemical Sensor for the Detection of Copper(II) in Drinking Water. Sensors **2019**, 19, 5246.
20. Camara, J. S.; Alves, M. A.; Marques, J. C. Changes in volatile composition of Madeira wines during their oxidative ageing. *Anal. Chim. Acta* **2006**, 563, 188-197.