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Towards the development of cascaded surface plasmon resonance POF sensors exploiting gold films and synthetic recognition elements for detection of contaminants in transformer oil

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ABSTRACT

The possibility of developing a multichannel optical chemical sensor, based on molecularly imprinted polymers (MIPs) and surface plasmon resonance (SPR) in a D-shaped multimode plastic optical fiber (POF), is presented by two cascaded SPR-POF-MIP sensors with different thicknesses of the gold layer. The low cost, the high selectivity and sensitivity of the SPR-POF-MIP platforms and the simple and modular scheme of the optical interrogation layout make this system a potentially suitable on-line multi-diagnostic tool. As a proof of principle, the possibility of simultaneous determination of two important analytes, dibenzyl disulfide (DBDS) and furfural (2-FAL), in power transformer oil was investigated. Their presence gives useful indication of underway corrosive or ageing processes in power transformers, respectively. Preliminarily, the dependence of the performance of the D-shaped optical platform on the gold film thickness has been studied, comparing two platforms with 30 nm and 60 nm thick gold layers. It has been found that the resonance wavelengths are different on platforms with gold layer of different thickness, furthermore when MIPs are present on the gold as receptors, the performances of the platforms are similar in the two considered sensors.

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1. Introduction

Bio and chemical sensors based on SPR in optical fibers have been shown to be able to play an important role in numerous relevant fields, including pharmaceutical researches, medical diagnostics, industrial applications, environmental monitoring, food safety and security, where fast, portable, low cost and rugged units are needed for early detection and identification [1–5]. Here the fiber core replaces the glass prism and couples the entrance light to the sensing element, giving a sensor which works in the wavelength interrogation mode and has advantages over the prism configuration such as miniaturization and integration, remote sensing, real time and in situ monitoring [6]. In general, the optical fiber is either a glass or a plastic one (POF). POFs are practically 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 advantage of using POFs is that the main features of POFs, that have increased their popularity and competitiveness for telecommunications, are exactly those that are important for optical sensors based on glass optical fibers, with the addition of simpler manufacturing and handling procedures. POF with

a large diameter are suited for sensors also for the great number of modes, the relatively easy splitting of the light beam and connection with other fibers. Also, experimental results on POF sensor indicate that the configuration with a fiber of large diameter exhibits better performance, with respect to a fiber with minor diameter, in terms of sensitivity and resolution even if not in terms of signal-to-noise ratio [7,8].

A number of experimental setups have been proposed in the recent years in order to excite the SPRs by an evanescent wave from an optical fiber [6–11]. Among them, a D-shaped multimodal plastic optical fiber obtained by an easy and reproducible polishing procedure has been demonstrated to be very helpful for sensor applications. In particular the combination of a D-shaped plastic optical fiber and a molecularly imprinted polymer (MIP) receptor is an effective way to obtain a highly selective and sensitive SPR optical sensor platform. Several examples of applications of this optical chemical sensor platform have been reported, as for example the selective detection of trinitrotoluene (TNT), for security applications [12], of furfural (furan-2-carbaldehyde) in power transformer insulating oil [13], and of L-nicotine [14] in clinical applications.

In this work we show the possibility of developing multiple analyte sensor systems based on SPR on the D-shaped plastic optical fiber platform, previously employed for single analyte determination in connection with molecularly imprinted polymers as receptors. Several

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approaches, based on parallel or serial connection have been previously proposed on the basis of theoretical and experimental investigation [15, 16]. The possibility to use surface plasmon resonance on plastic optical fiber with molecularly imprinted polymer (SPR-MIP-POF) sensors for multianalyte detection has been also discussed [17]. In [17] two similar optical sensors, with two specific MIP receptors, were considered. It has been shown that in that case only an experimental set-up with the two sensors in parallel is possible, since the surface plasmon resonances are the same for the two sensors.

Here an approach based on different platforms, each one specific for one analyte, and based on a gold layer of different thickness, is described. As a proof-of-principle the monitoring of the concentration of two interesting substances in the insulating oil of power transformers, is presented.

The power transformer is a key component of the Electric Transmission and Distribution system. Its integrity assessment is very complex but essential to avoid irreversible damages with consequent heavy impacts on maintenance costs and on T&D network services, due to outages. Among the causes which can lead to a transformer failure (i.e., hot spots, partial discharges), the accelerated degradation of its solid insulating system, i.e., oil impregnated cellulosic insulation materials, strongly depends on the operating condition of the transformer [18,19].

In power transformers the degradation of the dielectric parts begins much earlier than the predicted end-of-life of the transformer (foreseen as 30 years), due to an accelerated thermal ageing of both the insulating oil and the paper. While the regeneration of a degraded insulating oil is possible by appropriate treatments or even by its replacement with a new compatible oil [20], the refurbishment of degraded paper requires invasive and costly operations that must be necessarily performed by the manufacturer, because it can involve the total replacement of transformer windings. For this reason it is well established [21,22] that the end of useful life of a transformer is mainly determined by the thermal deterioration of paper and that a careful monitoring of the parameters linked to this process is of fundamental importance for utilities to check the “health” of the in-service transformers.

One of the main components of the insulation paper (i.e., Kraft paper) is cellulose, which consists of a long linear chain of β -D glucose molecules [22,23]. As the paper ages, its mechanical strength changes significantly because of degradation (depolymerization) of the cellulose chains; in a domino effect, the decrease of mechanical strength also reduces the ability of the transformer to withstand short circuit stress, confirming that these two properties are not mutually disjoint but are in synergy. For this reason, the mechanical strength of the paper is considered an important diagnostic parameter in transformers and its reduction down to 50% is assumed as an indication of the end-of-life of a transformer [21]. The viscometric test, according to the IEC 60450 [24], provides a reliable and direct measure of the degree of polymerization (DP) value but actually this method is not practical, because it requires a sample of paper from the transformer insulation system, which is impossible to access during regular operation. The indirect measure of the insulating paper decomposition products dissolved in oil, such as carbon dioxide and carbon monoxide (CO_2 and CO) [25, 26], methanol [21,27], furfural (furan-2-carbaldehyde, 2-FAL) and related furans is generally preferred. While CO and CO_2 can be generated by decomposition of the oil during long term oxidation too, methanol, furfural and furans are only formed by the processes of thermal degradation of the cellulose [21,25,28]. Their concentration in transformer oil is strictly correlated to the degree of polymerization of the paper [21, 25,26], as for instance in the case of Kraft insulating paper. Although methanol has been widely demonstrated to be very promising as a marker of ageing [21,27,28], currently the 2-FAL concentration is used worldwide as one of the main indicators to estimate the ageing of the paper in a transformer [21,25]. As the presence of furan compounds in oil is not related to the degradation of the oil itself, they can be used as chemical markers in transformer insulating oil to assess the overall degree of polymerization of cellulose with a high degree of confidence

[25,29]. Currently, common practice consists of periodic oil sampling from in-service transformers and in analysis usually performed in a laboratory far from the sampling site. It is carried out usually by chromatographic methods, such as for instance by high pressure liquid chromatography (HPLC) according to the IEC 61198 method [30]. This technique is quite complex, requiring the extraction of the substances of interest from the sample before the injection on the chromatographic column, the use of expensive equipment and specialized operators both for acquisition and for data analysis, and a long time period for obtaining the results.

Dibenzyl disulfide (DBDS) too is an important analyte in the control of transformer oil since it is commonly added to the transformer oils as an antioxidant. At the same time it is responsible for the corrosive properties of the oil, even at relatively low concentration [31–34]. Similarly to 2-FAL, the determination of its level in transformer oils is of paramount importance for diagnostic purposes i.e. to monitor the “health status” of the transformer, and a number of analytical methods for its determination are described in the literature [33]. Nevertheless, no sensors have been previously proposed, despite of the fact that this would be of interest for in situ monitoring.

SPR-POF-MIP sensors are good candidates for in situ detection of different diagnostic markers directly in the mineral oil matrix. This methodology potentially allows to overcome problems, caused by current practices, of periodical collection of oil samples from the transformer and application of more expensive and time-consuming standard analytical methods. Moreover, the possibility to use surface plasmon resonance on plastic optical fiber with molecularly imprinted polymer (SPR-MIP-POF), exploiting a parallel setup, for the simultaneous detection of two important analytes, namely dibenzyl disulfide (DBDS) and furfural (2-FAL), whose presence in the transformer oil is an indication of underway corrosive or ageing processes, respectively, has been already demonstrated [17].

In this work, a multianalyte device, based on two cascaded SPR-MIP sensors in POF, for simultaneous determination of DBDS and 2-FAL in transformer oil, is presented. It exploits gold layers of different thicknesses but not different metals, as theoretically suggested for another optical fiber set-up [15], due to the higher stability and inertness of gold with respect to other metals.

2. Materials and methods

2.1. Sensing method

SPR is a very sensitive technique for determining small refractive index changes at the interface between a metallic layer with a fixed receptor and a dielectric medium (solution with analyte).

In SPR sensors with spectral interrogation, the resonance wavelength (λ_{res}) is determined by the refractive index of the sensing layer (n_s). If the refractive index of the sensing layer is altered by δn_s , the resonance wavelength shifts by $\delta \lambda_{\text{res}}$. The sensitivity (S_n) of an SPR sensor with spectral interrogation is defined as [7–11]:

$$S_{n_s} = \frac{\delta \lambda_{\text{res}}}{\delta n_s} \left[\frac{\text{nm}}{\text{RIU}} \right] \quad (1)$$

For a particular bio-chemical optical sensor, the sensitivity is more conveniently defined as [1–5,35]:

$$S = \frac{\delta \lambda_{\text{res}}}{\delta C_{\text{analyte}}} \left[\frac{\text{nm}}{\text{M}} \right] \quad (2)$$

In other words, this sensitivity is defined as the shift in resonance wavelength per unit change in analyte concentration (C_{analyte}).

Owing to the fact that the vast majority of the field of the Surface Plasmon Wave (SPW) is concentrated in the dielectric, the propagation constant of the SPW is extremely sensitive to changes in the refractive

index of the dielectric itself. This property of SPW is the underlying physical principle of affinity SPR bio/chemical sensors. In the case of artificial receptors, as molecular imprinted polymers (MIPs), the polymeric film on the surface of metal selectively recognizes and captures the analyte present in a liquid sample so producing a local increase in the refractive index at the metal surface. The refractive index increase gives rise to an increase in the propagation constant of SPW propagating along the metal surface which can be accurately measured by optical means. The magnitude of the change in the propagation constant of an SPW depends on the refractive index change and the overlap with the SPW field. In the MIP layer, the SPW propagation is directly influenced by the refractive index change induced by the analyte binding.

The resolution (Δn) of the SPR-based optical sensor can be defined as the minimum change in refractive index detectable by the sensor.

The bio-chemical sensing applications require an SPR sensor's resolution value (Δn) of around (10^{-4} – 10^{-3}) RIU [1–5,35].

With spectral interrogation, this parameter definitely depends on the spectral resolution ($\delta\lambda_{DR}$) of the spectrometer used to measure the resonance wavelength in a sensor scheme. Therefore, if there is a shift of $\delta\lambda_{res}$ in the resonance wavelength corresponding to a refractive index change of δn_s , then resolution can be defined as [7–11]:

$$\Delta n = \frac{\delta n_s}{\delta\lambda_{res}} \delta\lambda_{DR} [\text{RIU}] \quad (3)$$

The signal-to-noise ratio (SNR) of the SPR sensor with spectral interrogation is defined as [7–11]:

$$\text{SNR}(n_s) = \left(\frac{\delta\lambda_{res}}{\delta\lambda_{SW}} \right)_{n_s} \quad (4)$$

where $\delta\lambda_{SW}$ is calculated as the variation of the full width at half maximum (FWHM) of the SPR curve. SNR is a dimensionless parameter strongly dependent on the refractive index (n_s).

2.2. Optical sensor platform

A plastic optical fiber with a PMMA core of 980 μm and a fluorinated polymer cladding of 20 μm is used. On the basis of experimental results,

the configuration based on a large diameter fiber is better in terms of sensitivity and resolution but not in terms of signal-to-noise ratio, SNR [7]. The optical sensor manufacturing implies the following simple steps:

- embedding the optical fiber without the protection in a resin block;
- removal of the cladding of a plastic optical fiber along half the circumference and of a short portion of the optical fiber embedded in a resin block. This gives a flat exposed surface of the core;
- spin coating an "optical buffer" (Microposit S1813 photoresist) on the flat part of the exposed core of the fiber;
- sputtering a thin gold film over the optical buffer.

The plastic optical fiber without jacket was firstly embedded in a resin block for polishing procedure. This operation was carried out with a 5 μm polishing paper in order to remove the cladding and part of the core of the fiber. After 20 complete strokes with an "8-shaped" pattern in order to completely expose the core, a 1 μm polishing paper was used for another 20 complete strokes with an "8-shaped" pattern. The final length of sensing region was about 10 mm.

Successively the optical buffer (Microposit S1813 photoresist) was spin coated on the sensing region. The sample was spun at 6000 rpm for 60 s to obtain a 1.5 μm final thickness of the photoresist buffer. It has been already verified [8] that the POF-SPR sensor with a photoresist buffer layer (with high refractive index) between core POF and gold film exhibits better performance in terms of detectable refractive index range and SNR. The refractive index, in the visible range of interest, is about 1.49 for PMMA, 1.41 for fluorinated polymer and 1.61 for Microposit S1813 photoresist.

Finally, in order to make two different optical sensor platforms, two different thin gold films were sputtered on two D-shaped POF platforms, by a sputtering machine (Bal-Tec SCD 500). The gold films were 60 nm (Au60nm) and 30 nm (Au30nm) thick and both presented a good adhesion to the substrate. Furthermore, two specific MIP layers were deposited on these different optical sensor platforms (with different gold layers) as receptors for the detection of 2-FAL and DBDS. The refractive index of the MIP, synthesized as reported below [12–14], is higher than 1.42 RIU, in the visible range of interest.

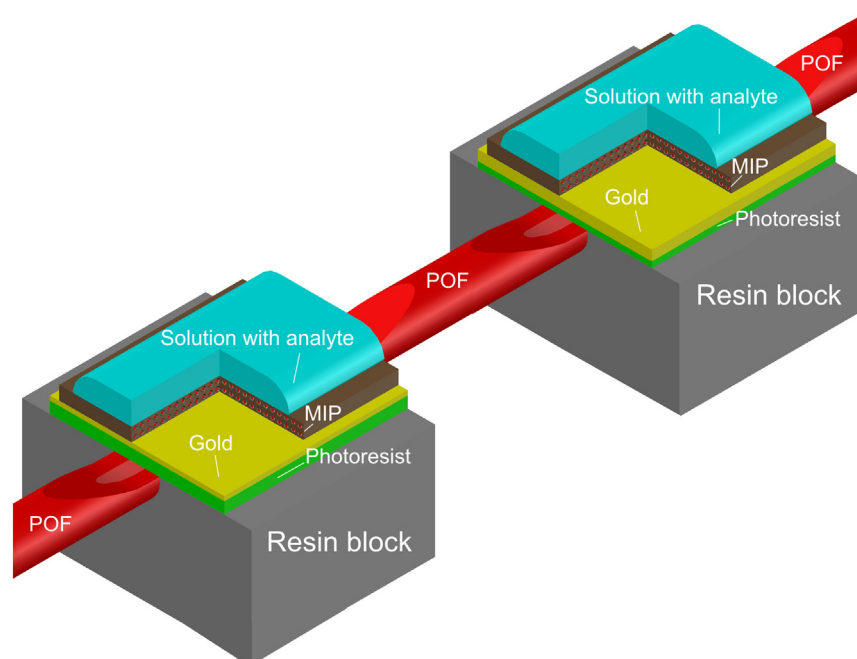


Fig. 1. Optical chemical multichannel sensor system based on cascaded SPR-MIP sensors.

2.3. Chemical receptors

The gold planar surface over the D-shaped POF (SPR active surface) was washed with ethanol and then dried in a thermostatic oven at 60 °C prior to deposition of the sensing layer, i.e. a specific molecularly imprinted polymer layer.

The prepolymeric mixture for MIP was prepared according to the classical procedure reported in [13,36] with only slight modifications. Divinylbenzene (DVB), the cross-linker, was also the solvent in which the functional monomer (methacrylic acid, MAA), and the template (furfural (2-FAL) or DBDS) are dissolved. The reagents were at molar ratio 1 (template):4 (MAA):40 (DVB). For example, a typical prepolymer mixture for the MIP specific for 2-FAL is composed of 20 μl of furfural, 80 μl of MAA and 1.4 ml of DVB. The prepolymeric mixture for the DBDS MIP had the following composition: DBDS as template (20 mg), MAA as functional monomer (30 μl), DVB as cross-linker (465 μl) and AIBN as the radical initiator (15 mg). The reagents were again at molar ratio 1 (DBDS): 4 (MAA): 40 (DVB). Notice that in both cases DVB is at the same time the cross linker and the solvent. This particular cross-linker was selected because of its hydrophobic characters. The mixture was uniformly dispersed by sonication (visually homogeneous solution) and de-

aerated with nitrogen for 10 min. Then the radical initiator AIBN (16 mg in the example described) was added to the mixture. Fifty μl of the prepolymeric mixture were dropped over the sensing region of the optical fiber and spun for 45 s at 700 rpm. Thermal polymerization was then carried out for 16 h at 70 °C. The template was extracted by 10 repeated washings with 96% ethanol.

2.4. Experimental setup

The experimental measurements for the characterization of the SPR-POF sensors have been previously carried out in different ways, i.e. spectral and amplitude mode. In this work we used a particular setup based on the spectral mode configuration, allowing serial (or cascade) detection as shown in Fig. 1. Only one spectrometer is needed, at which a combination of the spectra obtained at the two platforms, is finally recorded. This aspect is important because the spectrometer is the most expensive among all the devices present in the setup. The here used halogen lamp (HL-2000-LL, Ocean Optics) exhibits a wavelength emission range from 360 nm to 1700 nm, while the spectrum analyzer detection range was from 330 nm to 1100 nm. The spectral resolution of the

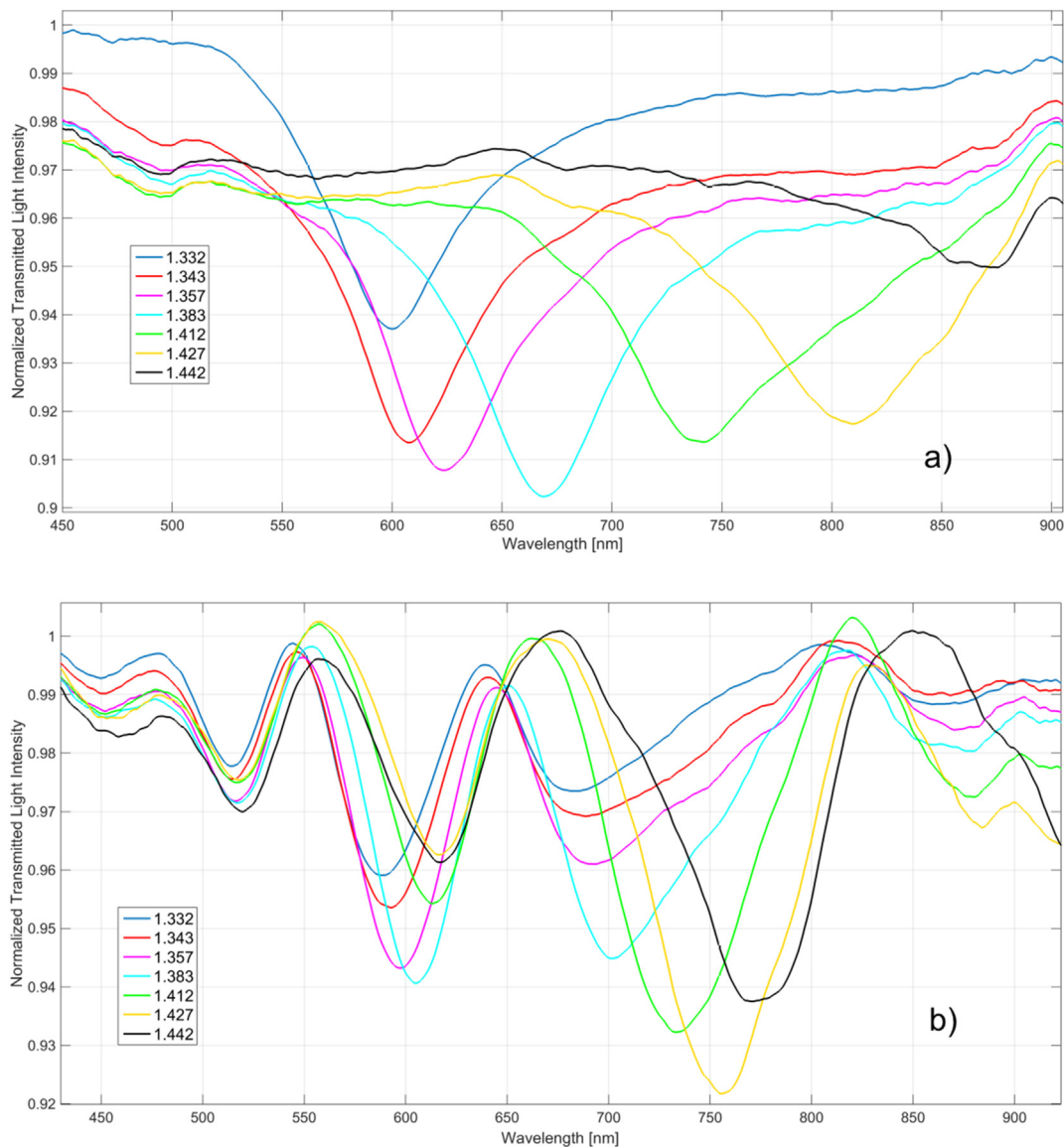


Fig. 2. Experimentally obtained SPR transmission spectra, normalized to the air spectrum, for different refractive index of the aqueous medium. Configuration with 60 nm thick gold layer (a), and with 30 nm thick gold layer (b).

Table 1

Parameters of the D-shaped optical sensor platform in a water-glycerin solution with RI = 1.427.

Optical platform	Resonance wavelength (nm)	Sensitivity (nm/RIU)	FWHM (nm)	SNR
30 nm thick gold layer	616.6	270	48.7	4.2
60 nm thick gold layer	809.5	2390	94.3	5.3

spectrometer (USB2000 + UV–VIS spectrometer, Ocean Optics) was 1.5 nm ($\delta\lambda_{DR}$).

The SPR spectra along with data values were displayed online on the computer screen and saved with the help of advanced software provided by Ocean Optics.

When the MIP receptor is present, the transmission spectra have been normalized to the spectra obtained in air before MIP deposition, in which not any plasmon resonance is excited, due to the refractive index range for which the platform here described is suitable [12–14].

2.5. Experimental procedure

The SPR transmission spectra are obtained by dropping 20 μ l of the appropriate solution on the platforms with MIPs and without MIP

(bare platforms). The steady state wavelength shift was obtained after 5 min incubation. The platforms were rapidly washed with hexane after each measurement. Each experimental value is the average of 5 subsequent measurements, taken after 5 min incubation with the respective standard deviations.

The two bare optical platforms (configuration without MIP) with different gold layer thickness were characterized independently. The solutions of glycerin in water were prepared, characterized in terms of refractive index by using an Abbe refractometer, then adopted as the sensing media. All the solutions were stored at 20 °C.

The MIP sensors were then simultaneously characterized in the cascaded configuration (see Fig. 1). The sample solvent was a mineral oil for electrical transformer (Nytro Libra), containing or not containing the selected analytes.

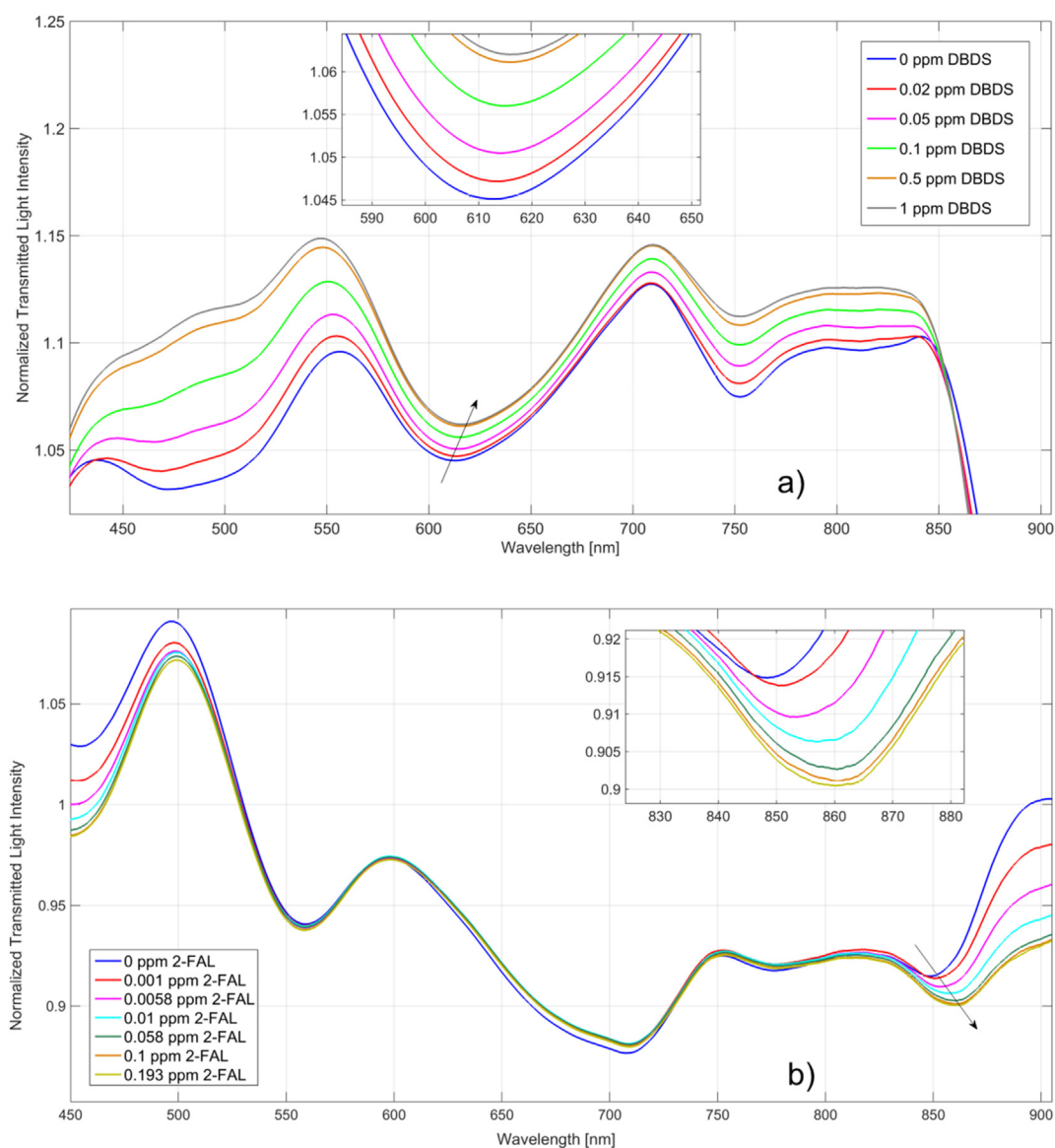


Fig. 3. a) POF-MIP sensor with 30 nm thick gold film: SPR transmission spectra for different concentrations of DBDS (ppm) in oil. b) POF-MIP sensor with 60 nm thick gold film: SPR transmission spectra for different 2-FAL (ppm) concentration in oil. Insets: zoom of resonance wavelengths.

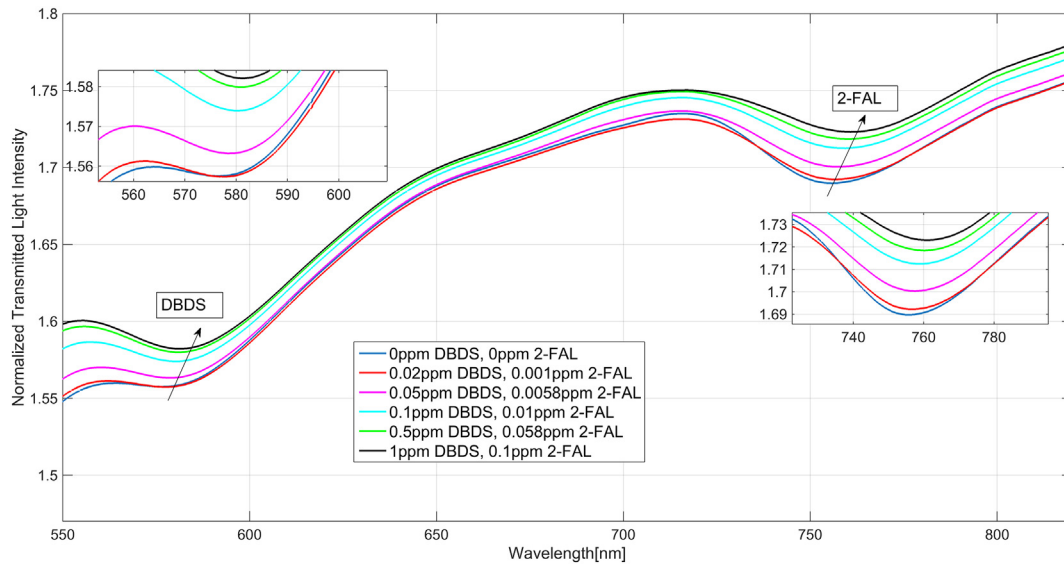


Fig. 4. Absorption spectra of the cascaded configuration at different concentrations of DBDS (30 nm thick gold layer sensor) and 2-FAL (60 nm thick gold layer sensor).

The possibility of performing measurement in a particularly convenient way for practical application, i.e. in a few μl drop, is offered by the shape of the optical platform here proposed, which presents a flat surface and can be easily maintained in an horizontal position (see Fig. 1).

3. Results and discussion

3.1. Influence of the gold film thickness on the optical platform performance

The surface plasmon resonance wavelength spectra at the bare D-shaped POF optical platforms with different gold layer thickness have been obtained independently. The normalized spectra are reported in Fig. 2 for 30 and 60 nm gold layers (Au30nm and Au60nm, respectively) and for liquid dielectrics with different RI (mixtures glycerine/water). Wavelengths higher than about 950 nm should not be considered since in the experimental apparatus here used the transmittance is very low in that range [8]. There is a striking difference between the spectra at all the considered liquid dielectrics dropped over gold layer. In particular, three main resonance dips are present for Au30nm, at around 510, 590, 690 nm in water, while only one for Au60nm, at 600 nm (see Fig. 2). This particular behavior should be ascribed to the highly multimodal structure of the fiber here considered. Analyzing the spectra at high RI, as for example at 1.427 (the refractive index of the MIP is higher than 1.42), it is evident from Fig. 2 that the resonance dip appears at 810 nm in the case of Au60nm, while at 518, 615, 755 nm in the case of Au30nm thick. Thus the peaks are well resolved, especially at high RI, roughly corresponding to the RI of the MIP here considered.

All the minima are shifted toward higher wavelengths at increasing RI, i.e. the resonance wavelengths are red-shifted. The dependence on the RI of the sensing layer is not linear over the entire range but just in a small interval. The sensitivity of the two sensors at RI = 1.427 are reported in Table 1, together with other characteristics of the resonance spectra (SNR and FWHM). As summarized in Table 1, the SNR is practically the same at Au60nm and at Au30nm, whereas the optical sensitivity is higher in the Au60nm case but the peak width is larger.

For both sensors here considered, the deepness of the peaks shows a particular behavior with RI: it seems to increase up to about RI = 1.39, then it decreases. Nevertheless the peaks are clearly localizable, even at the high RI of the MIP here used for recognition.

3.2. Detection of 2-FAL and DBDS in oil

The spectra obtained for the bare SPR platform (i.e. without MIP layer) with 30 nm thick gold layer at different RI (Fig. 2b) show that three main resonance dips are present, which are shifted to higher

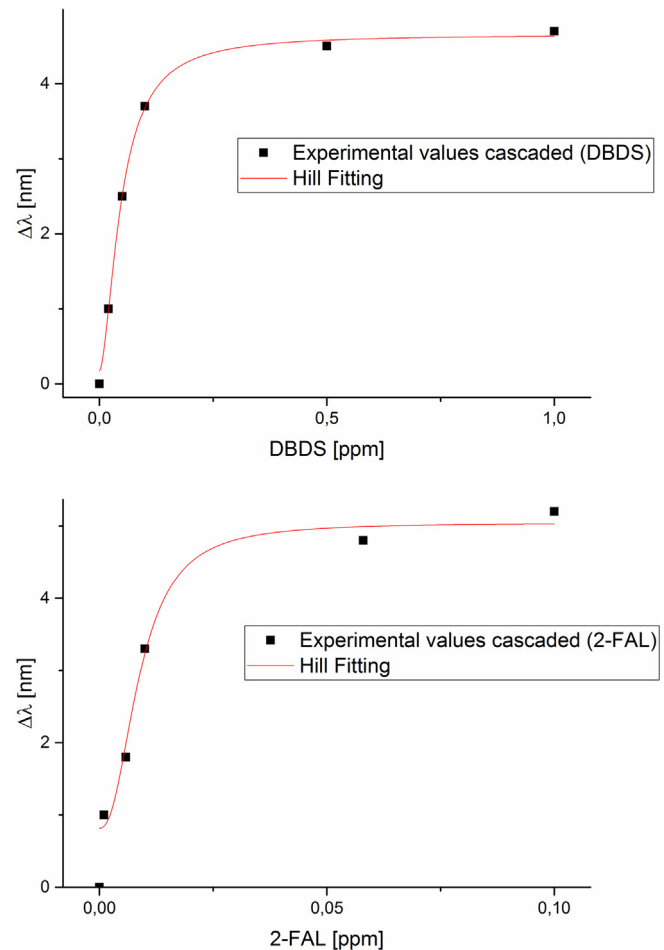


Fig. 5. Standardization curves for DBDS and 2-FAL, obtained from the resonance wavelengths of Fig. 4.

Table 2
Cascaded configuration of the DBDS and 2-FAL sensors: analytical parameters from the Hill fitting.

Sensors	$\Delta\lambda_{\max}$ (nm)		K_{aff} (M^{-1})		Sensitivity at low conc. (nm M^{-1})		LOD (M)
	Value	Std. dev.	Value	Std. dev.	Value	Std. dev.	Value
DBDS at 30nmAu	4.48	0.795	$5.16 \cdot 10^6$	$1.30 \cdot 10^6$	$2.32 \cdot 10^7$	$7.12 \cdot 10^6$	$6.76 \cdot 10^{-8}$
2-FAL at 60nmAu	4.229	0.843	$1.09 \cdot 10^7$	$3.09 \cdot 10^6$	$4.61 \cdot 10^7$	$1.60 \cdot 10^7$	$2.97 \cdot 10^{-8}$

wavelengths at increasing RI. In particular, especially at high RI, they are located at wavelengths well different from those of the resonance occurring for the bare sensor with 60 nm thick gold layer (Fig. 2a). These characteristics are very promising for a multianalyte detection based on in-series SPR-MIP sensors.

First of all, the spectra obtained individually for the two MIP sensors were considered, for the sake of comparison:

- Fig. 3a shows the absorption spectra of the stand-alone SPR-MIP sensor for DBDS, with 30 nm thick gold layer. The transformer oil is the liquid in contact, i.e. the dielectric layer, at different concentrations of DBDS. In the case of the 30 nm thick gold layer (DBDS sensor) it can be seen that only one dip is useful for detection, i.e. that at about 615 nm, which is red-shifted at increasing concentration of DBDS in the oil. In this case the red shifted SPR resonance is located in the middle of the spectral region of detection, i.e. at about 615 nm.
- Fig. 3b shows the stand-alone spectra of the SPR-MIP sensor for 2-FAL, with 60 nm thick gold layer. Here too only one useful resonance appears, at about 860 nm, which is red-shifted for increasing concentration of DBDS.

As previously described in the case of similar sensors [12,14], the SPR wavelength shift, with respect to the resonance wavelength at 0 ppm, have been fitted by the Hill equation, in order to determine the chemical parameters of interest.

In the case of DBDS detection the following values have been obtained: $K_{\text{aff}} = 3.47 \cdot 10^6$ (M^{-1}); Sensitivity at low concentration = $1.24 \cdot 10^7$ ($\text{nm} \cdot \text{M}^{-1}$); LOD = $2.94 \cdot 10^{-8}$ (M).

In the case of the 2-FAL sensor, with 60 nm thick gold layer, the chemical parameters of interest in the detection of 2-FAL, calculated by the Hill fitting, are: $K_{\text{aff}} = 1 \cdot 10^7$ (M^{-1}); Sensitivity at low concentration = $6.1 \cdot 10^7$ ($\text{nm} \cdot \text{M}^{-1}$); LOD = $4 \cdot 10^{-7}$ (M). These LODs, obtained individually for DBDS and 2-FAL, are similar to the values obtained by parallel configuration based on two identical optical platforms with 60 nm gold layer and two different specific MIPs [17].

From the spectra in Fig. 3, it can be seen that the resonance wavelengths of the two sensors are very different. Noticeably, this is in agreement with the findings for bare platforms (Fig. 2). Here too, for RI of the dielectric layer higher than 1.42, no resonance peaks appear around 615 nm for the Au60nm platform (see Fig. 2a) and no resonance peaks appear around 860 nm for the Au30nm case.

The peak around 615 nm (Au30nm sensor) can be used for the detection of DBDS. Whereas, 2-FAL can be determined with an MIP sensor with 60 nm thick gold layer positioned in series with the sensor for DBDS. The red shifted resonance at about 850 nm can be used for quantification of 2-FAL, since no resonance due to DBDS is present at this wavelength.

The normalized transmission spectra of the cascaded configuration, with the 2-FAL sensor following the DBDS one (see Fig. 1), are reported in Fig. 4 for different 2-FAL and DBDS concentrations. Two resonance dips are formed at around 580 nm and 760 nm, which are ascribed to DBDS and 2-FAL, respectively. This has been done by the comparison between the transmission spectra of the single compounds (Fig. 3) at the respective sensors. Notice that the resonance wavelengths do not

exactly correspond to those of the single compounds (Fig. 3), due to the fact that a higher-order modes filtering of the multimode fiber is produced in the D-shaped POF waveguide.

The dose-response curves at about 580 nm for DBDS and 760 nm for 2-FAL are shown in Fig. 5. The chemical parameters obtained by the Hill fitting, for the two analytes at the cascaded configuration, are reported in Table 2.

It can be seen that the relevant parameters are not significantly different from those obtained from the single analyte experiments. However the LOD of 2-FAL is significantly lower than that obtained by the individual experiments, probably due to the fact that here the resonance peak is in a much better position, i.e. near to the middle of the detectable resonance wavelength range.

A difference between the two considered analytes is in the respective linearity range, which is up to 0.02 ppm ($2 \cdot 10^{-7}$ M) for 2-FAL and 0.1 ppm for DBDS ($4 \cdot 10^{-7}$ M).

For both MIPs used in this work, different substances were considered for testing the selectivity. There isn't any specific adsorption of the considered substances on the MIP, because no resonance wavelengths shift is observed, although relatively high concentrations are considered.

For example, in the detection of DBDS, furfural (2-FAL) and diphenyl disulfide (DPDS) are impurities likely present in used transformer oils, and for this reason they are considered as possible interfering substances. The two considered interfering substances do not give any wavelength shift at MIP-POF sensor, so indicating that they are not adsorbed

4. Conclusions

Experimental results of cascaded SPR-MIP sensors, for the detection of two markers (DBDS and 2-FAL) directly in transformer oil, have demonstrated an attractive feature for industrial application. It has been shown that one POF-MIP sensor, based on a gold film 60 nm thick, combined with another POF-MIP sensor, with a different gold film thickness (30 nm), can be used in a cascaded configuration to monitor two refractive indices variations of MIP receptors in function of the amount of absorbed analytes, directly in power transformer oil. In this new configuration it is possible to use only one spectrometer, so obtaining a low cost multichannel optical chemical sensor system.

The width of the resonance peaks is particularly relevant in the case of cascaded multianalyte sensors, since evidently this limits the number of analytes which can be simultaneously determined. This aspect is very important when multimode plastic optical fibers are used, because the FWHM is very large. However, it has been shown that, in the experimental set up here investigated, it is sufficiently narrow to allow at least two analytes to be simultaneously determined.

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