

DETECTION OF VOLATILE ORGANIC COMPOUNDS BASED ON OPTICAL FIBRE USING NANOSTRUCTURED FILMS

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Abstract- An optical fibre sensor for detection of volatile organic compounds (VOCs) has been implemented. This device is based on a vapochromic material presented in the form of bright red powders, which suffers reversible changes in its optical properties when exposed to some organic vapours. The sensor head consists of a nano interferometer doped with the vapochromic material, built onto a cleaved ended multimode optical fibre by using the Layer by Layer Electrostatic Self Assembly Method (LbL). A reflection scheme was used, so the intensity modulated reflected signal is registered in order to study its response. Changes up to 3 dB in the reflected optical power were measured.

Index terms: optical fibre sensor; gas sensor; vapochromic material; Layer by Layer

I.INTRODUCCION

In last few years, many researching groups have been focusing their attention to the development of sensors towards detection of VOCs. Some of the most important targets for these devices are environmental applications, electronic noses, food or chemical industry [1]. They can help to determinate whether or not the fermentation process of alcoholic beverages is completed [2], or if the concentration in air of a chemical product is below the safety level for workers in a factory. Most of these sensors are polymer-based electronic devices: the amount of the VOC in the ambient and its reactivity with the polymer determine the sensitivity of the sensor. For example, in other works it have been used resistive sensors [3] to

measure swelling of the polymer; capacitive sensors [4, 5] to measure changes in polymer permeability, just to mention a few.

In this context, fibre optic sensors are a good alternative to electronic ones: some of these electronic sensors need to be heated at 400 °C to operate [6], and all of them need to be biased to work, so, as an electric signal is required, they are not recommended in environments where there is an explosion risk, as chemical plants. Besides, electromagnetic signals can produce severe interferences to electronic sensors, impeding them to operate properly. In order to solve these problems, optical fibre sensors shows passive nature, immunity to electromagnetic noise, small size and light weight, durability, remote operation or capability of multiplexing several sensors in one fibre. The most common operation principle of these sensors is the modulation of the light intensity produced by the substance to be detected [7]. The sensing element can be either the fibre itself or an external material fixed to the fibre; in any case, at least one optical property of the sensing material, such as the colour, the refractive index or fluorescence, should depend of the monitored substance in the surrounding environment.

In this work, a vapochromic complex, whose optical properties suffer changes in presence of volatile compounds, is used as sensing material. Following the LbL method, ionic doped monolayers with this complex are deposited onto the cleaved end of an optical fibre, giving rise to a nano-cavity sensitive to alcohol solvent vapors.

II. VAPOCHROMIC MATERIAL

Organometallic chemistry is a discipline that has been growing in interest in last few decades. It is well known that organic compounds are based on the ability of carbon to form bounds with other carbon atoms; this property in transition metals such as gold, silver or palladium, is studied by organometallic chemistry, developing complex with interesting applications [8].

For the preparation of suitable detector of VOCs, it is necessary to find a complex able to change some properties in presence of organic solvents. Changes in colour or in refractive index are easy to monitor with simple scheme consisting of a light source and an optical fibre device. Although there is a great number of complexes showing solvatochromism (change in absorbance properties when dissolved in different liquids), for the construction of VOCs sensors, it is more important other property, the vapochromism. This term was present firstly by Nagel and Mann and co-workers [9] to describe complexes that change the colour in presence of VOCs.

There is a family of complexes of general formula $[\text{AuAg}(\text{C}_6\text{F}_5)_2\text{L}]_n$, where L is a ligand molecule that can be pyridine, 2,2'-bipyridine, 1,10 phenanthroline, $\frac{1}{2}$ diphenylacetylene and other ligands [10,11], which change from different colour as orange or red to white in the presence of coordinating solvent as acetone, methanol or ethanol. In these cases, the polynuclear structure of starting compound $[\text{Au}_2\text{Ag}_2(\text{C}_6\text{F}_5)_4(\text{C}_6\text{H}_5\text{N})_2]$ disappears and a new anion-cation derivate is formed as a consequence of the solvent coordination to the silver centre, breaking both the gold-silver bounds and the gold-gold contacts, which are responsible of the initial colour. On the contrary, the final cation-anion structure shows white colour (see figure 1). Some fibre optic sensor based using this family of complexes, were characterized for VOCs detection [12]. Although a big quantity of solvent is necessary to provoke this effect completely, small ones in vapour phase can produce enough change in the refractive index to be detected.

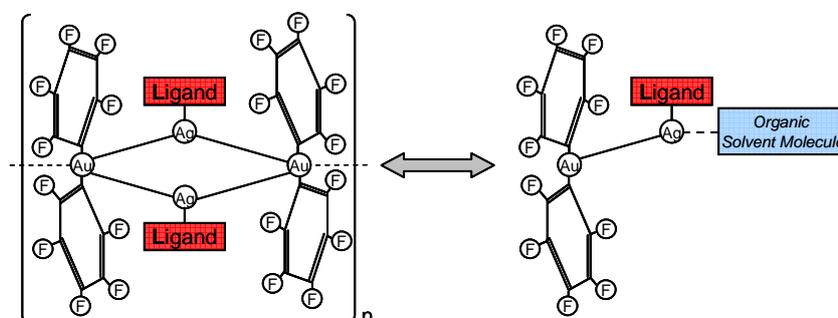


Figure 1. Molecule of the vapochromic material and its reaction in presence of organic vapours. Atoms size and chemical structure are idealized to make it more legible.

In this work, the gold-silver complex with pyridine ligands, has been employed for the detection of some VOCs. This material is present in form of bright red powders, and shows fluorescence at 575 nm when illuminated with light at 385nm.

III. EXPERIMENTAL SET-UP

The multimode optical fibre chosen has core and cladding diameters of 62,5 μm and 125 μm , respectively, and the end of which was cut with a Siemens S46999-M9-A8 precision fibre cleaver. The small size of the sensor head implies enormous advantages: just to mention a few, it shows low cross-correlation to temperature, robustness, reproducibility, fast response, and offers the possibility of using optical sources with low coherent length, etc. Furthermore,

it make possible to use an interrogating/detection scheme similar to the used in intensity based sensors.

The experimental reflection set-up employed is shown in figure 2. A Y coupler 50:50 was used to connect the system. This device has also a 62.5 μm core diameter, in order to avoid insertion losses.

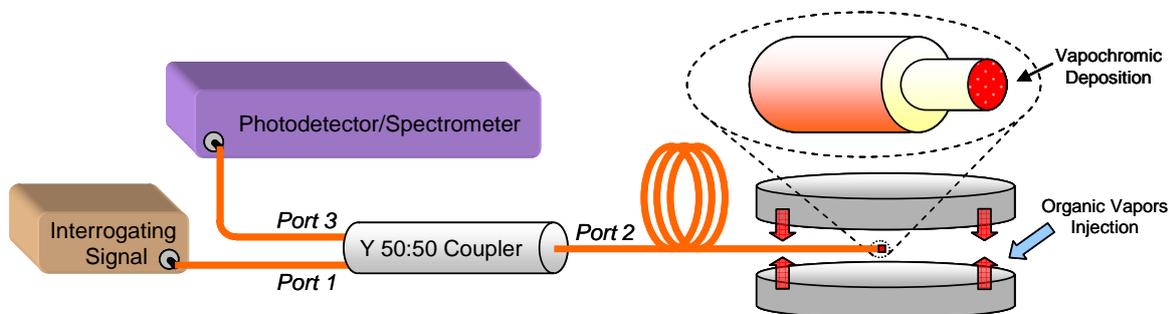


Figure 2. Set-up implemented to analyze the response of the fibre optic based sensor.

The sensor head is connected to port 2 and the other two ports are connected to the 850 nm LED source (port 1) and to the photodetector, 675RE from RIFOCS Corporation (port 3). When measuring the reflected optical power during the nanocavity construction, the sensor is stayed on air. In order to study the response of the device when exposed to VOCs, the sensor head is introduced into a hermetically closed chamber (diameter: 9 cm, high: 2 cm, volume: 275 cm³), where different VOCs are injected in liquid phase.

IV. NANOSENSOR IMPLEMENTATION

a. Layer by Layer method

The LbL method is a technique that is been used for deposition of several materials [13]; in the field of optical devices, it offers the possibility of building up two-beams Fabry-Perot nanocavities on fibres, with lengths less than a micrometer [14]. Simplicity and reproducibility are the most remarkable advantages offered by this method respect to other deposition techniques employed to implement optical fibre sensors such as, for example, dip coating [15-17] or Langmuir-Blodgett [18].

The LbL process has an iterative nature, so involves some steps: firstly, a substrate (in this case optical fibre), is cleaned and chemically treated with a mixture of sulphuric acid and hydrogen peroxide (3:1), inducing also a superficial negative charge density; then, the substrate is alternately dipped into solutions of cationic and anionic polymers, assembling

each time a nano film positively or negatively electrically charged with the previous one fixed (that is oppositely charged). The composition of each layer and the chemical variables of the polymeric solutions determine the final coating properties. The basic synthesis process is summarized in figure 3.

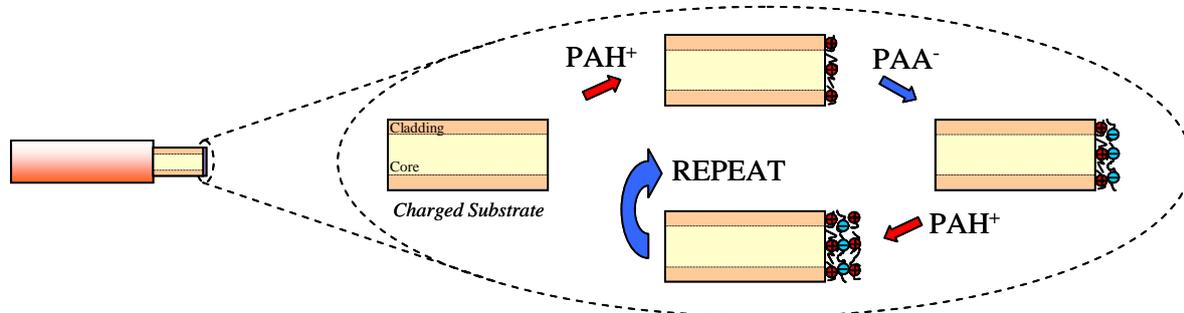


Figure 3. Main steps of the LbL method deposition process. Symbols are idealized and not intended to represent exactly the polyelectrolyte chains.

In this work, a solution of PAH (poly allylamine hydrochloride) was used as the polycation, and PAA (poly acrylic acid) as the polyanion. These polyelectrolytes are a good choice to develop nanostructures due to their ability to get their optical properties chemically modified by, for example, varying the pH [19, 20]. The resulting multilayer structure built up at the end of an optical fibre, behaves as a homogeneous optical medium, as each monolayer thickness is in same scale (nanometric) than the wavelength of the source used. The layers thickness obtained are below coherent length of LEDs, so the can be employed instead of LASERs as optical sources, reducing the cost of the final sensor system.

As previously commented, the layer structure of the coating forms a two-beams interferometer nanocavity on the optical wavelength scale [21]. With the set up described in figure 2, the evolution of the nanocavity can be registered just monitoring the reflected optical power each time a monolayer gets deposited, giving these measures a response similar to a Fizeau interferometer.

b. Doping the coating

The multilayer film structure had to be doped with the vapochromic material in order to obtain a VOC sensitive layer. First, it is necessary to decide in which polymer the vapochromic material has to be dissolved: PAH has an amine group would give electrons to silver atoms of the vapochromic molecule, acting as ligand (the same role than pyridine) [22]. The polycation is presented in hydrochloride form, so it has an acid behaviour: to avoid the

vapochromic molecule degradation, pH is raised to 7 for PAH solution; pH of the polyanion solution is also set at 7, in order to prevent potential problems in the construction of the structure [23].

Another additional drawback is that the vapochromical material is not soluble in water but in organic solvents. Some authors dissolved hydrophobic complexes in an organic water-soluble solvent, yielding to a hydrophilic mixture [24]. In this case, the vapochromic material is solved in ethanol, and this is diluted in pure water: final solution shows the same colour and fluorescence that presented the material in form of powders, and hence can be added to the PAH solution.

The solute concentration for both polycation and polyanion solutions is 10 mM, and the proportion between the vapochromic complex and ethanol is 1 mg/ml; 600 μ l of this solution are added to 20 ml of water, mixing it with the PAH solution, yielding the final polycation-vapochromic mixture.

c. Nanocavity construction

A multilayer structure of form $[\text{PAH}^+(\text{Vap})/\text{PAA}^-]_n$, where n indicates the final number of bilayers, was built up onto a cleaved ended pigtail optical fibre; a total of 25 bilayers were deposited. Just to prevent the interference of ethanol traces in the final nanostructure, the sensors were 1 hour at 50°C (see figure 4.a).

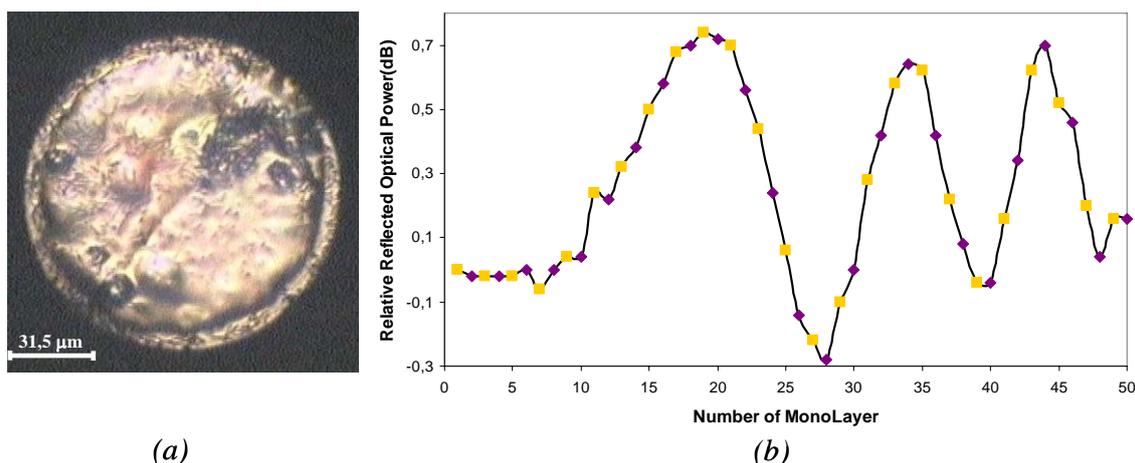


Figure 4. (a) Detail of a sensor head after the curing process. (b) Construction curve of the sensor for the polycation (square points) and polyanion (rhombus points).

The experimental results obtained during the build up of the multilayer structure process are shown in figure 4.b: the curve represent the relative optical power for each polymer layer. The

interferometric phenomenon has been monitored, so a nanocavity has been constructed at the end of the fibre. There are no differences bigger than 0.05 dB between each layer, so the structure has an adequate uniformity.

An increase in layers thickness can be observed counting the number of monolayers per period: to complete the first one, 26 monolayers are needed, for the second, 14, and for the third, just 10. These means that layers get thicker and the reason could be the vapochromic material bounded to the polycation chains.

V.RESULTS AND DISCUSSION

a. Spectral analysis

Spectral study has been used to measure vapochromic fluorescence characterise registering the emission spectra, and sensor response to different VOCs. To realise this analysis, the same reflection set-up shown in figure 2 has been used, connecting a CCD Spectrometer PC2000 connected to port 2, a LED at 385nm to port 1 when measuring the vapochromic material fluorescence; finally, a white light to source is used as optical source to study sensor absorbance spectra.

The fluorescence measurements are done to ensure that the vapochromic material is fixed in the sensor head: as this material shows fluorescence at 575 nm when is excited with a light source at 385 nm, if the sensor head is illuminated with a led at this wavelength, a fluorescence signal would confirm that the vapochromic material is successfully doping the nano cavity.

After dissolving the complex first in ethanol and then in water, the final solution maintain the colour of the powders and fluorescence; when the PAH solution is added to the vapochromic one, it loses its colour and becomes transparent, and when it is excited with a light source at 385 nm, the fluorescence peak emission changes to 525 nm. This confirms that there is an interaction between the polycation and the vapochromic complex; as there is still fluorescence, the vapochromic complex has not been destroyed by the acid behaviour of the PAH solution. These spectra can be observed in figure 5.

A valley in the absorbance spectra of the sensor around 530nm would corroborate that there is vapochromic material doping the interferometric structure, as it would be due to the fluorescence emission from the vapochromic complex. This will be shown in next section.

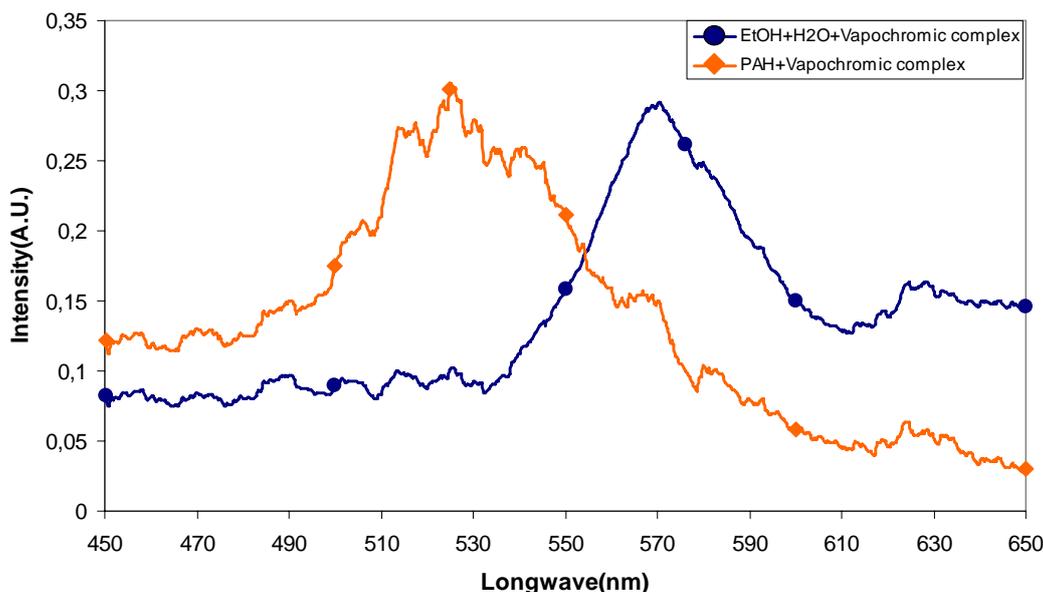


Figure 5. Reflected fluorescence spectrum from the vapo chromic complex solutions, when using a led at 385 nm.

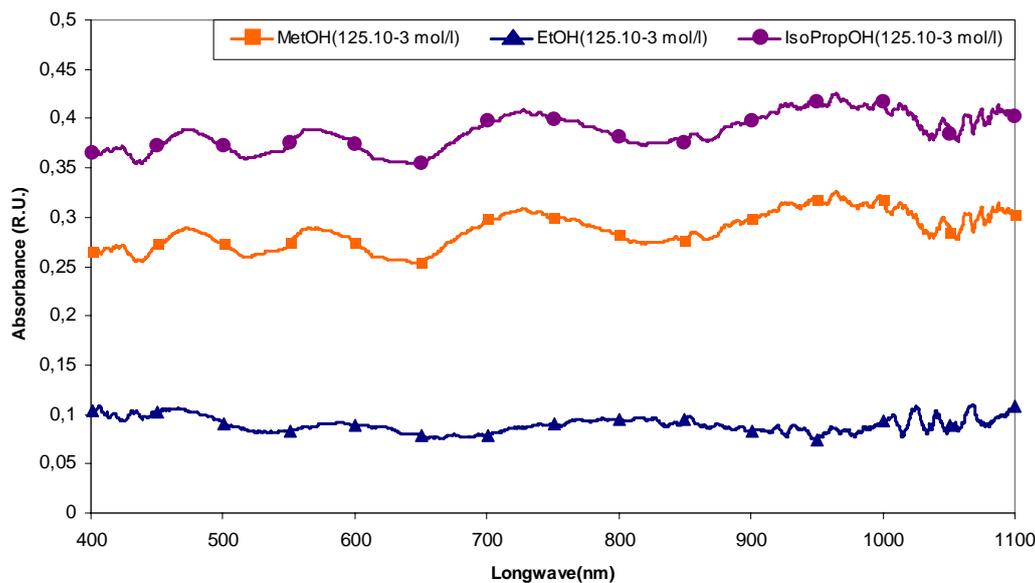
a.2. Absorbance spectra

In all cases, the absorbance will be expressed in relative units defined by the formula:

$$A = -\log\left(\frac{S_{\lambda} - D_{\lambda}}{R_{\lambda} - D_{\lambda}}\right) \tag{1}$$

where S_{λ} is the optical power received from the sample, D_{λ} is the optical power of the dark reference signal, and R_{λ} is the optical power measured from the reference signal, all of them at wavelength of λ .

Figure 6 shows the optical absorbance of the nano cavity when exposed to three different organic vapours: concentrations for each case are $86 \cdot 10^{-3} \text{ mol/l}$ for ethanol, $125 \cdot 10^{-3} \text{ mol/l}$ for methanol and $40 \cdot 10^{-3} \text{ mol/l}$ for isopropanol. In case of ethanol and methanol, the curve is quite similar in shape, but the methanol one has bigger amplitude; a valley in amplitude around 525nm can be observed, near from the fluorescence emission of the vapo chromic complex solved with the polycation, confirming definitely that there is vapo chromic product doping the interferometric cavity. This phenomenon is also presented with isopropanol, but is not so noticeable: the absorbance spectrum for isopropanol is almost flat and has the lowest amplitude.



Absorbance spectra of the sensor head for each VOC after 40 minutes exposure.

Ethanol and methanol can be discriminated only by information from the amplitude, but they both show a different spectra shape compared to the isopropanol one; figure 6 also shows that there is a wide spectral region where the optical interrogating signal could be used, which gives the system an important degree of flexibility and the possibility of implementing a sensor network.

The absorbance spectra is register 40 minutes after the VOC is introduced to chamber where the sensor is, which is longer than results reported in other VOCs sensors [25]. This is could be because of several factors as the curing applied to the sensor head, the doping process, the complex reaction time, but the most important, is the time needed by the VOC to get evaporated inside the chamber. This last effect can be inferred from the following figures by seeing the almost instantaneous recovery time of the sensor once the chamber is open. The influence of these factors is under study and will be shown elsewhere in further works.

b. VOC assembly analysis

The first step in the measuring process is the injection of the organic solvent into the chamber where the sensor is placed; after some minutes, the VOC gets vaporized and the atmosphere inside the chamber becomes saturated, starting the adsorption process at the nanocavity surface, producing changes in its optical properties, and so, altering the reflected optical power collected. Once this signal is stabilized, the chamber is opened and the optical power recovers its original value. This cycle has been done twice for ethanol ($86 \cdot 10^{-3}$ mol/l) and

methanol ($125 \cdot 10^{-3}$ mol/l), showing that the response is repetitive and that it could be used to discriminate between these vapors. These results are shown in figure 7.

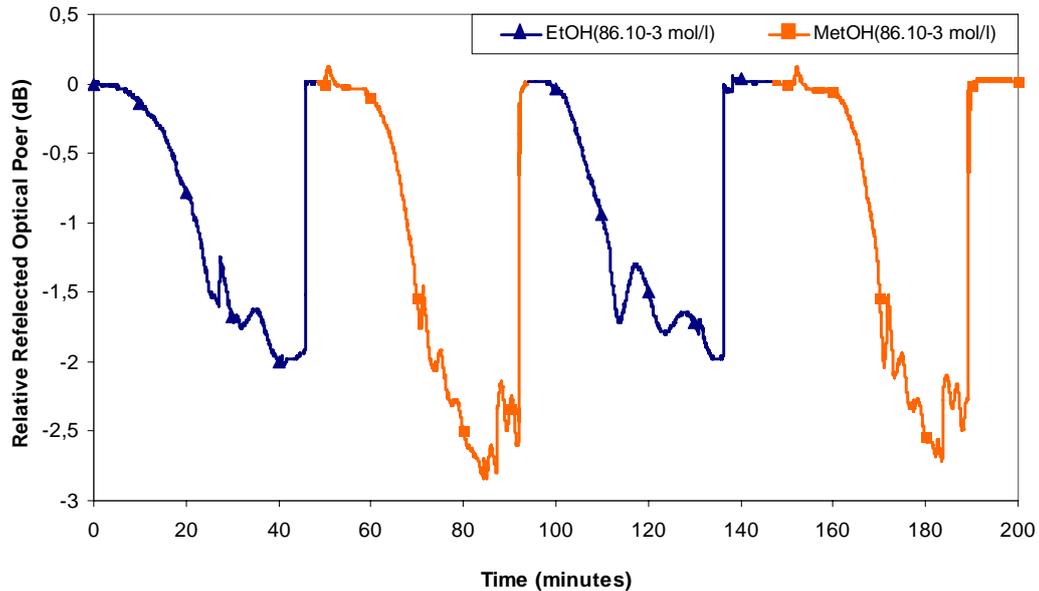
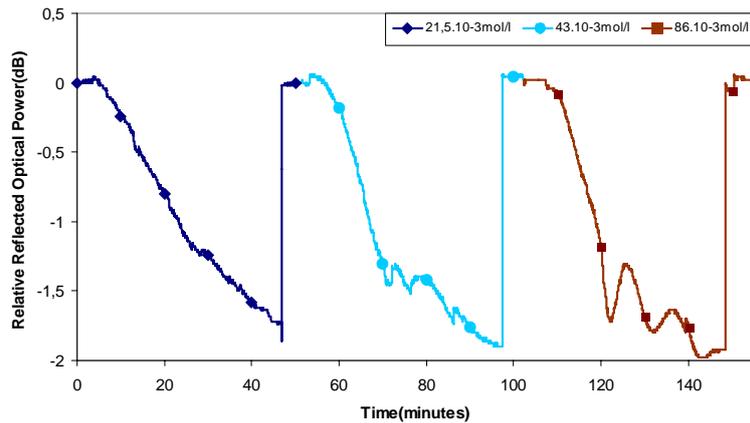


Figure 6. Comparison between the response of the sensor for ethanol and methanol.

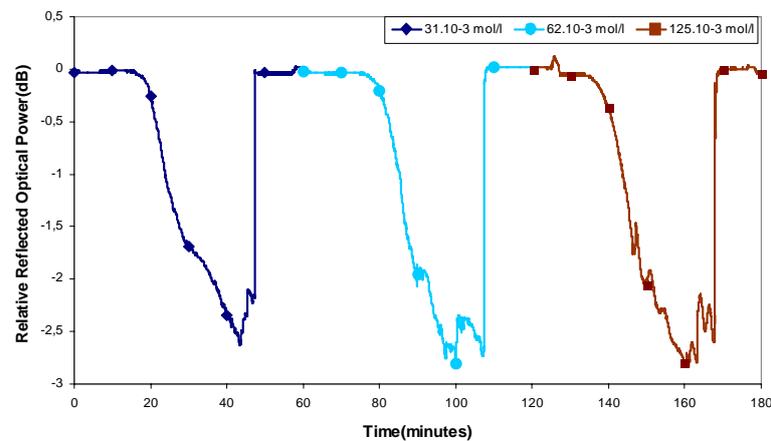
c. VOC individual analysis

The response of the sensor for different concentrations of ethanol and methanol vapours has been studied discriminately: figure 8.a shows the ethanol sensor response with concentrations of $21.5 \cdot 10^{-3}$ mol/l, $43 \cdot 10^{-3}$ mol/l and $86 \cdot 10^{-3}$ mol/l. From this figure, it can be observed that the optical reflected power level does not differ much between them, only 0.3 dB, being time response the main difference between each measure: as the concentration decreases, the optical reflected power begins to fall later, and needs more time to get stabilized. This gives at least three possible alternatives to distinguish among concentrations: it is possible to measure the optical reflected power at one certain time since the ethanol is introduced to the chamber; another possibility consists on registering the time that the sensor needs to get its lower level, and finally, the fall slope can also be used as parameter to discriminate between concentrations.

Figure 8.b shows the sensor response when it is exposed to different methanol concentrations. The methods shown above are able to discriminate between different concentrations in this case too. It is remarkable that the sensor has been used for one month, and no degradation in the doped nanocavity and neither variation in its behaviour were observed.



(a)



(b)

Temporal response of the sensor when exposed to different ethanol (a) and methanol (b) concentrations.

VI.CONCLUSIONS

An optical VOCs sensor has been experimentally implemented. This device is based on a vapochromic material which can detect some VOCs and determinate the concentrations of their vapors. The technique employed to make it is LbL method, which offers a high reproducibility and a very efficient use of the vapochromic complex, opening the way to further investigations to improve it. Using a cleaved ended multimode fibre, the fabrication process takes only one day. The instrumentation necessary is very simple and the optical source is a LED, so the total cost of the sensor system is very low.

Acknowledgements

This work was funded in part by the Spanish Ministry of Education and Science - FEDER TEC2006-12170/MIC Research Grant and Government of Navarra-Feder Euroinnova Research Grants.

REFERENCES

- [1] P. Mielle, F. Marquis, C. Latrasse, "Electronic noses: specify or disappear", *Sensors and Actuators B*, Vol. 69, pp. 287-294, 2000.
- [2] A.M. Taurino, D. Dello Monaco, S. Capone, M. Epidani, R. Rella, P. Siciliano, L. Ferrara, G. Maglione, A. Basso, D. Balarano, "Analysis of dry salami by means of an Electronic nose and correlation with microbiological methods", *Sensors and Actuators B*, Vol. 95, pp. 123-131, 2003.
- [3] A. Hashimoto, T. Hibino, K. Kobayashi, et al., "A resistor-type sensor for the detection of CO in reformed gases", Vol. 71, No. 6, pp. 398-401, 2003.
- [4] E.L. Tan, W.N. Ng, R. Shao, et al., "A wireless, passive sensor for quantifying packaged food quality", *Sensors*, Vol. 7, No. 9, pp. 1747-1756, 2007.
- [5] E.P. O'Brien, T.C. Ward, "Transient signal analysis using complementary metal oxide semiconductor capacitive chemical microsensors", *Analytical Chemistry*, Vol. 78, No. 1, pp. 279-290, 2006.
- [6] K. Tamaki, S. Sonoki, T. Tamaki, K. Ehara, "Measurement of odour after in vitro or in vivo ingestion of raw or heated garlic, using electronic nose, gas chromatography and sensory analysis", *International Journal of Food Science and Technology*, Vol. 43, pp. 130-139, 2008.
- [7] C. Elosua, I.R. Matias, C. Bariain, F.J. Arregui, "Volatile Organic Compound Optical Fibre Sensors: A Review", *Sensors*, Vol., 6 No. 11, pp. 1440-1465, 2006.
- [8] R. Uson, A. Laguna, P.G. Jones, J.M. Sheldrick, "Synthesis and reactivity of bimetallic Au-Ag complexes. X-ray structure of a chain polymer containing the moiety $(F_5C_6)_2Au(AgSC_4H_8)_2$ ", *Chemical Communications*, pp. 1097-1098, 1981.
- [9] C.E. Buss, C.E. Anderson, M.K. Pomije, C.M. Lutz, D. Britton, K.R. Mann, "Structural investigations of vapochromic behavior – X-ray single-crystal and powder diffraction studies of $[Pt(CN\text{-}iso\text{-}C_3H_7)_4][M(CN)_4]$ for M= Pt or Pd", *J. Am. Chem. Soc.* Vol. 120, No. 31, pp. 7783-7790, 1998.
- [10] A. Luquin, C. Bariain, E. Vergara, et al., "New preparation of gold-silver complexes and optical fibre environmental sensors based on vapochromic $[Au_2Ag_2(C_6F_5)_4(phen)_2]_n$ ", *Applied Organometallic Chemistry*, Vol.19, No. 12, pp. 1232-1238, 2005.
- [11] C. Bariain, I.R. Matias, I. Romero, J. Garrido, M. Laguna, "Behavioral experimental Studies of a novel vapochromic material towards development of optical fibre organic compounds sensor", *Sensors and Actuators B*, Vol. 76, pp. 25-31, 2001.

- [12] C. Bariain, I.R. Matias, C. Fernandez-Valdevieso, F.J. Arregui, M.L. Rodriguez-Mendez, J.A. de Saja, "Optical fibre sensor based on lutetium bisphthalocyanine for the detection of gases using standard telecommunication wavelengths", *Sensors and Actuators B*, Vol. 93, pp. 153-158, 2003.
- [13] Y. Liu, A. Wang, R. Claus, "Molecular Self-Assembly of TiO₂/Polymer Nanocomposite Films", *Journal of Physical Chemistry B*, Vol. 101, No. 8, pp. 1385-1388, 1997.
- [14] F.J. Arregui, I.R. Matias, Y. Liu, K. Lenahan, R. O. Claus, "Optical fibre nanometer-scale Fabry-Perot interferometer formed by the ionic self-assembly monolayer process", *Optics Letters*, Vol. 24, No. 9, pp.596-598, 1999.
- [15] C. Elosua, C. Bariain, I.R. Matias, A. Rodriguez, E. Colacio, A. Salinas-Castillo, A. Segura-Carretero, A. Fernandez-Gutiérrez, "Pyridine vapors detection by an optical fibre sensor", *Sensors*, *in press*.
- [16] C. Bariain, I.R. Matias, I. Romeo, M. Laguna, "Detection of volatile organic compound vapors by using a vapochromic material on a tapered optical fibre", *Applied Physics Letters*, Vol. 77, No. 15, pp. 2274-2276, 2000.
- [17] F. J. Arregui, Z. Ciaurriz, M. Oneca, I.R. Matias, "An experimental study about hydrogels for the fabrication of optical fibre humidity sensors", *Sensors and Actuators B*, Vol. 96, pp. 165-172, 2003.
- [18] W. Hu, Y. Xu, S. Liu, S. Zhou, P. Zeng, D. Ben Zhu, "The gas sensitivity of Langmuir-Blodgett films of a new asymmetrically substituted phthalocyanine", *Sensors and Actuators B*, Vol. 56, pp. 228-233, 1999.
- [19] W.Y. Yuan, H. Dong, C.M. Li, "pH-Controlled construction of chitosan/alginate multilayer film: Characterization and application for antibody immobilization", *Langmuir*, Vol. 23, No. 26, pp. 13046-13052, 2007.
- [20] S.S. Shiratori, M. F. Rubner, pH-Dependent Thickness Behavior of Sequentially Adsorbed Layers of Weak Polyelectrolytes, *Macromolecules*, Vol. 33, pp. 4213-4219, 2000.
- [21] E. Tjipto, J. F. Quinn, F. Caruso, "Layer-by-layer assembly of weak-strong copolymer polyelectrolytes: A route to morphological control of thin films", *Journal of Polymer Science Part A – Polymer Chemistry*, Vol. 45, No. 18, pp. 4341-4351, 2007.
- [22] R. Usón, A. Laguna, M. Laguna, B.R. Manzano, A. Tapia, "Bimetallic Gold-silver Pentachlorophenyl Complexes", *Inorganica Chimica Acta*, Vol. 101, No. 3, pp. 151-153, 1985.

- [23] N. S. Zacharia, M. Modestino, P.T. Hammond, "Factos influencing the interdiffusion of weak polycations in multilayers", *Macromolecules*, Vol. 40 No 40. , pp. 9523-9528, 2007.
- [24] J. Chen, H. Luo, W. Cao, "Interaction of diazoresins and sulfonate containing polyelectrolytes", *Polymer Internacional*, Vol. 49 No. 4, pp. 382-386, 2000.
- [25] C. Bariáin, I. R. Matías, C. Fdez-Valdivielso, César Elosúa, A. Luquin, J. Garrido, M. Laguna, "Optical fibre sensors based on vapochromic gold complexes for environmental applications", *Sensors and Actuators B*, Vol. 108, pp. 535-541, 2005.