

# Fluorescence dip-probe POF sensor for Lead determination in contaminated soil extracts

David Izquierdo<sup>1</sup>, Mar Puyol<sup>1</sup>, Ignacio Garcés<sup>1</sup>, Iñigo Salinas<sup>1</sup>, M. Angeles Losada<sup>1</sup>, Javier Mateo<sup>1</sup>, Laia Rivera<sup>2</sup>, Julián Alonso<sup>2</sup>, Alfredo Villalobos<sup>3</sup>, Francisco Valdés<sup>3</sup>

<sup>1</sup> Photonic Technologies Group, I3A, Universidad de Zaragoza, Zaragoza, Spain.

<sup>2</sup> Dept. Analytical Chemistry, Universitat Autònoma de Barcelona, Barcelona, Spain.

<sup>3</sup> Instituto Tecnológico de La Laguna, Torreón, Coahuila, México.

## Abstract

A novel fluorescence dip-probe POF sensor has been simulated, fabricated and tested for Lead determination in contaminated soil extracts. The sensor is based on the special POF characteristics (NA and size core) and on a lead-selective chemically active membrane with a new synthesized fluorophore. The dip-probe has been optimised by simulations, improving the fluorescence collection. The sensor has been characterised chemically, presenting a fully reversible response with good enough sensitivity and detection limit. The sensor has been also applied to the lead determination in real samples with promising results.

## 1. Introduction

The use of POF (Polymer Optical Fibres) in opto-chemical sensing applications is increasing, due to their special optical characteristics such as their electromagnetic immunity and compared to silica based fibres lower cost, easier-handling, higher flexibility, wider core size and larger numerical aperture, which make them suitable for their use in fluorescence-based sensors. In this paper, a fluorescence dip-probe POF sensor for the measurement of lead concentration has been fabricated. Lead is one of the most toxic metals [1] found in the environment.

A miniaturised fluorescence sensor based on a flow cell, which contained a membrane with a fluorescent dye was previously studied [2]. Light coming from a laser was injected into the membrane, where the fluorescent dye changed its fluorescence properties according to the interaction of an ionophore in the membrane with the lead present in aqueous solutions. Although it featured some advantages such as the use of a flow injection analysis (FIA) system, it was a bulky design which prevented its in-situ application. In order to keep away the electronics from the sensing area, improving the sensor portability and easy-handling and allowing the in-situ measurements, a fluorescence dip-probe POF sensor based on the same optode has been designed, optimised, fabricated and tested. A POF is used to guide the excitation light from the source to a small sensing area, where the optode is deposited, and another POF is used to collect the light back to the electronics, where it is processed. For the

POF dip-probe optimisation, a simulation program based on dye surface sampling has been also developed. With this program different configurations of the POF fibres (distance to the fluorescent dye and the angle between the fibres) and the influence of the POF characteristics (numerical aperture and radiation pattern) on the system operation have been simulated.

The fluorescent optode has been formulated and optimised for lead determination in the mentioned optical set-up. It consists in a plasticized PVC membrane, which combines a new hemicyanine dye as an acidochromic fluorophore and a commercial lead ionophore. This system has been applied to measure the lead concentration in acetic extractions of contaminated soils samples from Torreón (México).

## 2. Experimental System

The complete system consists of an emitting diode-laser, the opto-chemical dip-probe sensor and the detection system (figure 1). The sensor is based on POF and on a chemically active membrane. The detection system includes a filter to reject the excitation wavelength, the wide-area photodetector and the lock-in amplification.

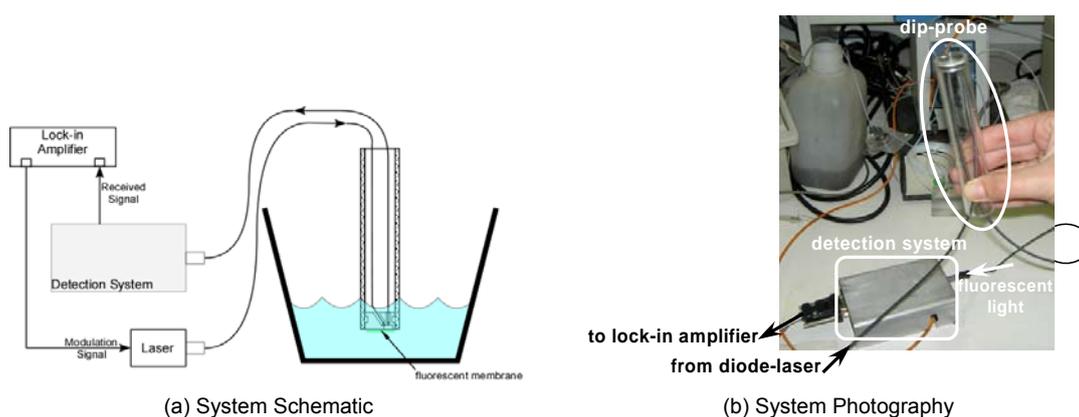


Fig. 1. Complete scheme (a) and photograph of the developed system (b).

### 2.1. Dip-Probe Sensor

Three main parts of the Dip-Probe Sensor can be distinguished (Figure 2): (1) the injection POF, which guides the excitation light from the Laser, (2) the glass window, where the optode is deposited on, and (3) the collection POF, which collects the fluorescent light back to the electronics. This optical set-up will be optimised with the simulation program to improve the fluorescence collection.

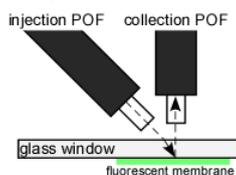


Fig. 2. Dip-Probe Schematic

## 2.2. Optode

The membrane contains a commercial lead ionophore, an anionic additive to maintain electroneutrality, and an acidochromic fluorophore. Its operation mechanism is easy: the commercial lead ionophore interacts with the analyte (in this case  $Pb^{2+}$ ) and the fluorophore releases protons to maintain the electroneutrality, changing its fluorescence characteristics (as shown in Figure 2.a). More detailed descriptions of the response mechanisms can be found in the literature [3].

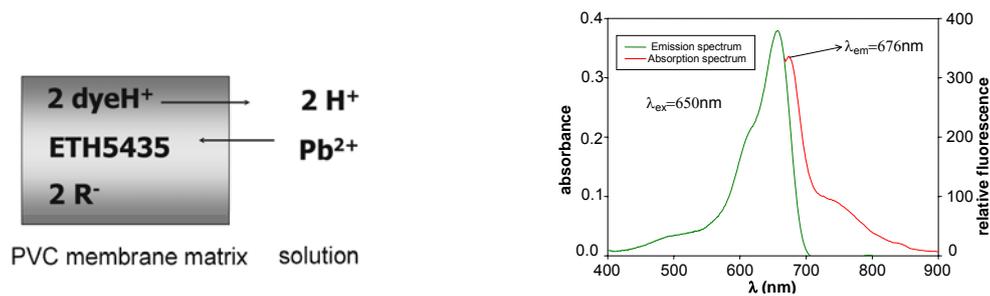


Fig. 3. (a) Cationic exchange, where ETH5435 is the commercial lead ionophore and R<sup>-</sup> is the anionic additive. (b) Absorption and Fluorescence Spectra of the fluorophore.

The fabricated optode was used in a previous work [2] and it is based on a new synthesized anilino-cyanine dye. The absorption and fluorescence spectra of the fluorophore are shown in figure 2.b and they define and limit the optical system and its components.

## 2.3. Measurement System

The measurement system includes the diode-laser, the reception system and the lock-in amplifier. The diode-laser wavelength matches the excitation band of the fluorophore (653nm) and is modulated with a sinusoidal signal generated by the lock-in amplifier. The detection system consists of a pair of lenses to collimate the light beam, so it can be filtered by an optical filter (fixed at the fluorescent wavelength at 680nm) to eliminate the excitation wavelength. The filtered light reaches a PIN photo-detector whose electrical output is taken to the lock-in amplifier to improve the SNR of the measurements. The schematic system is shown in figure 4.

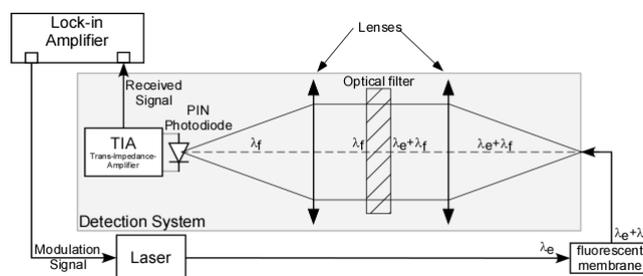


Fig. 4. Scheme of the measurement system

### 3. Dip-Probe Sensor simulation and optimisation

To optimise the design of the dip-probe, a simulation program based on dye surface sampling has been implemented using MATLAB<sup>®</sup>. The optical set-up used in this sensor can be seen in figure 5, where the collection POF (out) is placed normally to the surface and the injection POF (in) at a phi angle. The design parameters are the distances from the fibres to the surface, the angle between the fibres and the Numeric Aperture or their Radiation Pattern. The POF radiation pattern has been measured as in [4] and included in the program because it depends on the light source, the length and the NA of the POF.

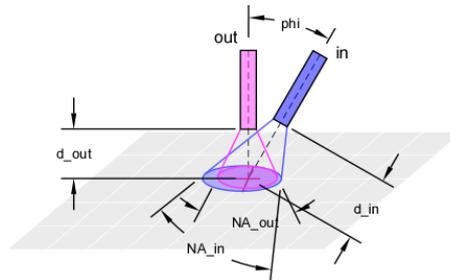


Fig. 5. Schematic of the fibres configuration in the simulation program.

The program supposes that the dye has a negligible thickness and it can be approximated as a superficial dye. To ease the calculations the surface is homogeneously sampled. The program firstly calculates the excitation power received by each surface sample due the injection POF (figure 6.a). Secondly the program calculates the portion of the fluorescent light emitted by each sample that enters into the collection POF (figure 6.b, collection efficiency). Finally, the collected fluorescent power is obtained as a result of these two magnitudes and the fluorescence efficiency of the sample (figure 6.c).

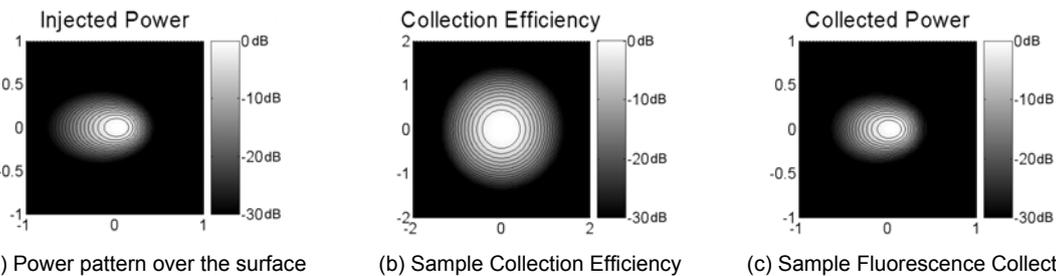


Fig. 6. Summary of the program operations (all of them are relative to the maximum and the lines are 2dB separated)

#### 3.2. Simulations

The angle between the fibres is fixed to 45° because it is the optimal angle to minimize the excitation wavelength interference reducing the direct reflection in the membrane. Due to the radiation isotropy of the fluorescence, this angle is not critical and the system only loses 0.29dB from the optimal angle, which would be near 0°.

The first parameter to be optimized is the NA of the fibres. The original system employed an injection fibre with a GRIN lens (NA≈0.008) and lenses for the collection. For this new system

the simulations predict (figure 7) an optimal configuration using the minimum NA available for injection and the possible largest NA for collection. According to this we chose, the PMU-CD1002–22-E (NA=0.32) for the injection and the ESKA-PREMIER-GH4001 (NA=0.50) for the collection; this results in a collection efficiency up to 8%.

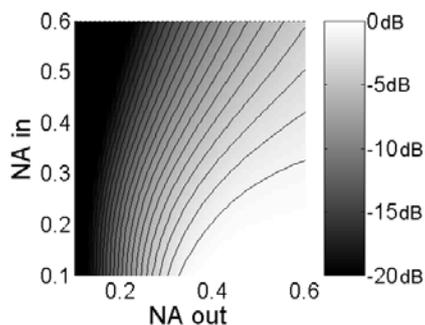


Fig. 7. Maximum Relative Collected Power Vs. NA (the lines are 1dB separated)

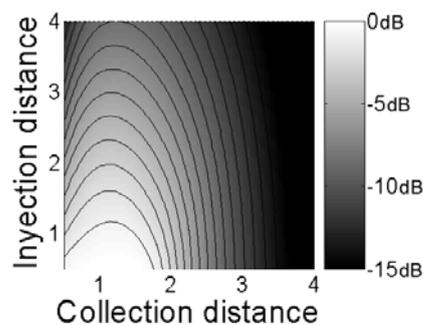


Fig. 8. Maximum Relative Collected Power Vs. Fibres distances to the surface (the lines are 1dB separated)

The last system parameters to be optimized are the distances from the fibres to the membrane surface. The simulation determines (figure 8) that the optimal distance from the injection fibre to the surface is equal to 1.2 times the POF core radius, and the collection fibre has to be placed as near as possible to the surface. Due to physical POF dimensions limitations and taking into account that the collection distance is more critical than the injection, the injection fibre is placed to 2.5 times the POF core radius and the collection at 1.2 times, losing about 4.25dB.

#### 4. Characterisation of the analytical response and application

The optical set-up for the lead-selective fluorescence dip-probe characterisation is shown in figure 1. The analytical response characteristics of the device have been first evaluated by performing different calibration curves using standard solutions and achieving a good enough sensitivity (-80.36uV/concentration decade) and a detection limit of 9.3ppm of  $Pb^{2+}$  (Figure 9). Furthermore, the response was fully reversible.

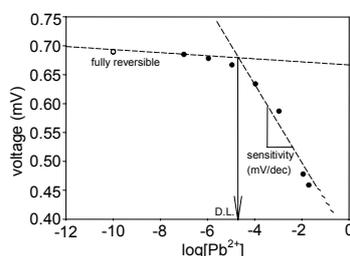


Fig. 9. Calibration curve to determine sensitivity and detection limit and to evaluate reversibility

Some metal interferences have been also evaluated, which are supposed to be found in environmental samples, by the Fixed Interference Method (FIM) and the selectivity constant  $K^{pot}$  has been determined as a parameter, which relates the response of the probe with and without the interfering ion [3]. Only  $Cd^{2+}$  slightly interferes in the response and  $Cu^{2+}$  makes it irreversible

by poisoning the employed dye.

In order to evaluate the feasibility of the proposal to environmental samples, it has been applied to the lead determination of some samples coming from the surroundings of a mining company in Torreón (Coahuila, México). The obtained results show the suitability of the lead selective dip-probe to the in-situ determination in real samples as they contain a negligible concentration of  $\text{Cd}^{2+}$  and no  $\text{Cu}^{2+}$  ions are present (Table 1). The paired t-test has been applied in order to compare the results obtained with the lead-selective dip-probe to those obtained by the ICP-OES method. It reveals that there are no significant differences between them. A greater number of samples are currently being analysed using the probe and the standard method ICP-OES in order to establish the applicability of the developed system.

Sample id.	Lead-selective dip-probe [ $\text{Pb}^{2+}$ ] $\cdot 10^{-5}$ (M)	ICP-OES [ $\text{Pb}^{2+}$ ] $\cdot 10^{-5}$ (M)
1	8.67	5.12
2	10.5	18.3
3	4.79	2.99
4	2.32	2.32

Table 1. Obtained results using the proposed probe and the standard method.

## 5. Conclusions

A novel fluorescence dip-probe POF sensor has been presented. The sensor is based on the special POF characteristics (NA and size core) and on a lead-selective chemically active membrane. The sensor has been characterised chemically, presenting a fully reversible response with good enough sensitivity and a detection limit of 9.3ppm of  $\text{Pb}^{2+}$ . The first results in real samples present a promising in-situ sensor.

## References

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