Fiber optic refractometric configurations for environmental sensing

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Abstract: - The implementation of refractometric based fiber optic sensors for environmental monitoring is discussed. Several sensing head configurations and interrogation schemes are presented and compared in the framework of different biochemical sensing applications. Results are presented demonstrating the suitability of this technology to monitor a diversity of chemical and biological parameters of environmental significance.

Key-Words: - Optical fiber sensors, refractometry, interferometry, chemical sensors.

1 Introduction

The need for complete and real time information about a variety of parameters is presently more important than ever in a diversity of complex systems ranging from industrial processes, aeronautic applications to complete ecosystems. In this context, the demand for new sensor technology capable of real time remote operation in electromagnetic or chemically hazardous environments is growing steadily.

The combination of optical fibers with optical sensing mechanisms has many characteristics that make it a promising alternative to standard technologies. Remote real time operation, multiplexing ability, miniaturization and immunity to electromagnetic interferences are some of the most appealing characteristics that motivate a growing scientific community. From such efforts it results that, presently, fiber optic sensing is already a growing industry, particularly dedicated to structural health monitoring in civil engineering, oil industry and aeronautics. In these demanding fields sensors for physical parameters like, strain, temperature, pressure and vibration have proven to be reliable choices[1].

On the other hand, sensing of chemical and biological parameters using fiber optic technology is an area in need for further developments to reach the industrial stage. While a huge diversity of sensing techniques has been successfully demonstrated in the last 30 years, very little has reached the market [2, 3].

Biochemical sensing typically requires that radiation interacts with the external media, either directly with a given analyte or by means of an auxiliary indicator dye. This makes it far more complex to design sensing systems with long term reliability.

Some of the most appealing techniques regarding sensitivity and specificity rely on the use of luminescent indicators. Probes to detect virtually any molecule can be designed for sensing based in quenching, energy transfer, proton transfer or electron transfer mechanisms [4]. Some interesting examples of successful applications include explosive detection, sensing of heavy metals or CO₂ detection. Nevertheless, only a few selected sensors are available as products for parameters such as oxygen and pH. While some of the intrinsic problems of luminescence based sensor like, leaching, photobleaching and temperature dependence have reported solutions, some limitations hinder further developments. A diversity of excitation sources, detectors and filters are needed to address the wide variety of spectral characteristics of luminescent probes. Furthermore such wavelength ranges demand for the use of specialty optical fibers and optoelectronics, severely limiting its compatibility with standard fiber optic industry.

Direct spectroscopy of gas absorption lines is an attractive solution in this regard. Nevertheless, most relevant gases absorb in the infrared (3 to 10 µm), and only a handful such as CO₂, methane and H₂S, can be detected by monitoring its higher harmonics in the telecom window (1,3 µm to 1,7 µm)[5].

In this context, label free solutions are very attractive. Such approaches do not interfere with the analyte properties and require, instead, the design of sensing layers that experience a refractive index change in its presence. This can be achieved by using biomolecules with a natural affinity to the target, or chemical species having analyte specific ligands. The combination of such membranes with refractive index sensors can therefore provide attractive solutions for biochemical sensing [6]. Possible platforms rely in
interferometry, surface plasmon resonance (SPR), and modified waveguides and fiber gratings. While SPR is one of the most successful (and sensitive) mechanisms for label free sensing, being presently incorporated into commercial bench top tools, the delicate nature of the sensing probe fabrication difficult its application in robust fiber optic based solutions [7]. Other fiber based solutions, on the other hand, typically require etching or tapering of the fiber, in order to increase the evanescent interaction with the external media or the sensing layer [8]. More recently, long period gratings offer an alternative for evanescent sensing without compromising the fiber integrity. Nevertheless, features like operation in transmission and high sensitivity to temperature still compromise its widespread application [9].

In this paper, we present several fiber optic based configurations for refractive index sensing with suitable characteristics for environmental sensing (namely, operation in reflection, high sensitivity, good fiber integrity and compatibility with multiplexing schemes). Results obtained in different biochemical sensing applications are presented demonstrating the suitability of standard fiber optics and telecom optoelectronics for environmental sensing.

2 Fiber optic probe configurations

Considering a wide range of possible configurations for refractive index sensing, those that are interferometric in nature are potentially more sensitive. A very simple and robust interferometric configuration can be obtained by simply coating the distal end of an optical fiber with the sensitive layer (figure 1a). In situations where the sensitive material refractive index provides enough contrast, the film at the fiber end constitutes a miniature Fabry Perot cavity where the reflections at the fiber/film and film/external medium interfere. When the layer refractive index changes, in the presence of the analyte, the interferometric output can be related with its concentration. While this is a very simple approach, some problems hinder it widespread application. In one hand, the optical power resulting from Fresnel reflections, considering the typical refractive index contrasts, is very low, seriously compromising the power budget of systems using multiple sensors. On the other hand, simple solutions such as wavelength multiplexing are not compatible with this configuration. Also, the film thickness necessary to obtain a meaningful spectral output, considering operation in the telecom wavelengths, typically exceeds several microns. This results in long diffusion times and slower sensor responses.

In order to obtain a similar Fabry Perot cavity effect, but being able to use thinner films, gaining at the same time multiplexing ability, we recently proposed a FBG based Fabry Perot cavity [10]. This was obtained by writing a low reflectivity FBG at cm distance from the distal end of the fiber (figure 1b). In this fashion, a refractometer is obtained with a unique spectral band corresponding to the FBG band and with an interferometric output whose visibility depends on the external wavelength. By coating the distal end of such a probe with an analyte sensitive material, a configuration is obtained, where the phase of the interferometric pattern depends on the analyte concentration [11]. Still, the optical power arising from such probe is limited to Fresnel reflections. Furthermore, in this situation, the interaction length with radiation is limited to the film thickness.

To obtain evanescent interaction over longer lengths, and hence increased sensitivity, LPG based configurations can be addressed. While reported LPG based sensors typically operate in transmission mode, a simple arrangement with FBGs can improve the system characteristics. We have recently demonstrated that by strategically combining, both geometrically and spectrally, two FBG and an LPG, a high sensitivity temperature and refractive index probe can be obtained that is operated in reflection and compatible with wavelength multiplexing schemes[12]. The sensing head configuration is shown in figure 1c. It consists of an LPG followed by two FBG whose spectral lines are placed in opposite sides of the LPG resonant response. In this situation, light reflected by the FBG crosses the LPG twice doubling sensitivity (see figure 2). Furthermore, it
was shown that by monitoring the ratio of the two FBG reflected power, and following its wavelength, it was possible to measure simultaneously refractive index and temperature. Refractive index resolution was approximately \(2 \times 10^{-5}\). Therefore, coating such probes with adequate layers will provide multiplexable sensitive chemical sensors.

![Figure 2. Schematic representation of the relative spectral arrangement of the Hybrid LPG-FBG configuration, for two distinct external refractive index values.](image)

Further increase in sensitivity is possible by exploring LPG interferometers (figure 1d). Placing a mirror a few cm after a 3 dB LPG, introduces the possibility to recombine light that travels by the core (reference arm) and by the cladding (sensing arm). In such configuration, all the fiber length that goes from the LPG to the mirror is sensitive to refractive index. In this way, interferometric sensitivity can be combined with long interaction lengths providing very high sensitivity. Such system is suitable to be interrogated and multiplexed using white light interferometry and coherence addressing.

Presently, other strategies to obtain sensitivity enhancements are being investigated that include the combination of the devices just described with partial etching of fiber tips, and combination of standard fiber with multimode and microstructured fibers to obtain compact and sensitive modal interferometers.

### 3 Interrogation schemes

The way the sensor signal is read out determines the kind of instrumentation needed and, ultimately, a great share of system cost. While in laboratorial conditions, the nature of the spectral output of most interferometric configurations justifies the use of optical spectral analyzers, the cost and delicate nature of such instruments prevent their widespread used in field applications.

With the development of FBG based sensing systems, new instruments capable of discriminating spectral shifts have become available that are portable and robust. Such is the case of laser scanning units like FS4200 from Fibersensing. With this instrument, the spectra of reflected signals can be analyzed with 1 pm resolution. In some of the applications described in this work, LabView based software programs were developed that enable the use of this unit to discriminate spectral shifts, calculate envelope visibility and perform some intensity based ratiometric measurements. This way, with a single system, and using some virtual instrumentation, a diversity of sensors systems could be implemented.

In spite of all, the cost of a single unit is still high and only justifiable when a large number of sensors are addressed. In addition, some of the interferometric configurations developed are compatible with high sensitivity interrogation techniques that can be implemented with lower cost. Such is the case of white light interferometry based techniques. Using broadband optical sources to illuminate interferometric sensing heads enables to read out its spectral shifts in the electrical domain. For this it is necessary to use a reading interferometer that, having its phase modulated, generates an electronic carrier. Furthermore, by tuning the path imbalance of the readout interferometer with the sensing interferometer, enable to address the sensor spectral shifts as phase shifts of the electronic carrier. Using such systems, an increase in sensitivity of at least one order of magnitude can be obtained as opposed to direct wavelength reading. Also, by using sensors with different path imbalances it is possible to address several sensors with the same system simply by scanning the path of the receiving interferometer.

We have recently demonstrated the use of fiber optic Michelson interferometer to interrogate different LPG based modal interferometers [13]. While very high sensitivity could be obtained, it was verified that significant phase drift was also observed that resulted from environmental influences on the reading interferometer. While packaging and thermal stabilization can greatly reduce this problem, such approach will add to system complexity and cost.

More recently, a Mach-Zhender readout scheme was implemented instead that enables differential measurements to be performed by analyzing simultaneous its two out-of-phase outputs. To obtain full immunity to spurious environmental effects, a sensing probe, and a reference probe, with identical characteristics must be used though. In spite of this added requirements, it was verified that system stability and reliability greatly increases, reducing the need for advanced packaging. In addition, the possibility of differential measurements to be performed between probes with different sensitivities to different analytes, opens up very interesting possibilities.
4 Results and applications

The combination of the different sensing heads and the interrogation methods described establishes a versatile platform for fiber based refractive index sensing that can be adapted and optimized for different purposes. In this context, different sensing membranes were developed for specific applications.

The technologies described are being explored with the goal of establishing a set of sensing systems suitable for environmental surveillance, particularly, addressing water quality. In this context, sensors for detection of cyanobacteria in water courses were developed. In particular, molecular imprinting and sol-gel technologies were combined to obtain sensitive layers that experience refractive index changes in the presence of Microcystin-LR, a widely studied hepatotoxin that cause serious health problems and can lead to dead. For assessment of membrane viability, the sensor was tested in the simplest tip Fabry Perot configuration.

The spectral output of the sensing head as a function of the toxin concentration is shown in figure 3. From this data a sensitivity of $12.4 \pm 0.7 \text{ nm L}^{-1}$ could be estimated. Considering that the spectral shift can easily be monitored with sub nanometer resolution the sensor is quite suitable to operate with great sensitivity around the World Health organization maximum recommended limit which is $1 \text{ µg L}^{-1}$.

![Figure 3 – Spectral response of MIP tip Fabry Perot to changing concentration of the toxin Microcystin-LR.](image)

Comparison of the sensor response with the one obtained with non-imprinted polymer demonstrated some selectivity (factor of two) that, nevertheless, needs improvement. The results present are quite promising, however, as MIP technology allows obtaining layers with selectivity at the molecular level of virtually any substance. In this context, the combination of such technology with refractometric fiber optic systems is an excellent platform for multiparameter environmental sensing.

In the context of developing a sensor for the determination of volatile fatty acids (VFA) for application in the optimization of anaerobic digestion processes, a FBG based Fabry Perot cavity was explored [11]. A 2 cm cavity obtained by writing a low reflectivity ($-4\%$) FBG near the fiber tip, was coated with a sol-gel based membrane containing polyvinylpyrrolidone. In this fashion, it was observed that the cavity spectral output, interrogated using a FS2200 Braggmeter from Fibersensing, was dependent on acetic acid concentration. The interrogation of the same sensor using a Fiber Michelson interferometer and a pseudo-heterodyne demodulation scheme allowed performing real time measurements (see figure 4) with a sensitivity of $-90 \text{ deg/% v/v}$ and a resolution of 0.2 % v/v in the 0.6 % to 3 % v/v range. More recently, the same membrane was tested in a LPG based Michelson interferometer, and a resolution of 0.01 %v/v was obtained using direct spectral analysis. These numbers clearly indicate that the right combination of sensing membrane and refractometric configuration can be used to suit any application in terms of operation range and sensitivity.

![Figure 4 – Real time response of FBG Fabry Perot probe to dynamic changes in acetic acid concentration.](image)

While most of the configurations described suffers from temperature dependence of their spectral features, several compensation schemes involving simultaneous measurements of the analyte and temperature can be implemented. Such was the case of the hybrid FBG-LPG configuration described in figure 1c. In the case of configuration 1b, on the other hand, it is possible to know the temperature by the spectral position of the fringe envelop, while the analyte information is retrieved from the relative fringe position.

However, when considering interferometric interrogation schemes, different approaches have to be addressed for temperature compensation. Using the Mach-Zhender interrogation scheme described in section 3, it is possible to perform differential measurements that can eliminate simultaneously several cross sensitivities such as temperature and bulk refractive index. For this purpose, however, careful design of the sensing head is needed. To
assess the effectiveness of the interrogation scheme, the system was tested using standard FBG as temperature/strain sensors. In an effort to dematerialize the instrumentation associated with the interrogation scheme, a virtual demodulation scheme was implemented in Labview environment that eliminated the need for function generators, lock-in amplifiers, filters and electrical spectrum analyzers. With the tools developed, furthermore, it was possible, at the switch of a virtual button to choose one of several heterodyne and pseudo-heterodyne demodulation schemes. Furthermore, comparison of the hardware based system with the virtual system (DAQ board and PC) showed very similar performances.

The results obtained showed impressive common mode rejection, eliminating most sources of noise. Placing the reference probe at a constant temperature, measurements could be made with the sensing probe with a resolution of 0.012°C, an order of magnitude better than standard spectral analysis. On the other hand, when sensor and reference were placed in the same probe, even temperature changes in excess of 50°C could be totally compensated. The differential system was used to implement a calorimeter to identify substances by detection of the temperature changes occurring during its evaporation. For this purpose unknown samples must be submitted to a temperature ramp while the temperature difference between the sample and a reference substance is monitored. Using this system it was possible to observe very accurately the evaporation of acetone and methanol in a mixed sample clearly demonstrating system viability (figure 5).

The performance observed indicates that, using refractometric probes with sensitive layers in such differential scheme can allow very sensitive chemical measurements to be performed free of environmental perturbations.

5 Conclusions

In this work a brief review fiber optic sensors for environmental applications was given. Several aspects regarding the implementation of label free biochemical sensors using standard optoelectronics were address. Practical examples of sensing head design, interrogation methods and practical applications were described. Results obtained clearly indicate that, given the possibility of designing a membrane that experiences refractive index changes in the presence of a target analyte, the necessary tools exist for the implementation of environmental sensing systems based in standard optoelectronics.

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