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Chapter 15

Optical Fibers to Detect Heavy Metals in Environment: Generalities and Case Studies

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1. Introduction

The fiber optic sensors can be used to create a truly distributed chemical sensing capability for selectively detecting metal compounds by spatial and temporal acquisition over large distances in the subsurface. In addition the fiber optic sensors have several advantages such as small size, light weight, immunity to electromagnetic interference (EMI), high temperature performance, large bandwidth, high sensitivity, and environmental ruggedness (Krohn, 1988). Most current technologies capable of detecting contaminants use strategically placed sensing or monitoring devices. This works reasonably well if plausible event location is known, hence settle recording vast amounts of benign data over time until the appearance of the suspected event. This approach remains limited for application in large spatial scales in the geo-environment and subsurface. A simple approach is to suppress all the benign data by triggered transmittal of the signals only at the spatial and temporal vicinity of the event. This, in essence the "truly distributed" sensing capable of delivering the event signal "*wherever*" and "*whenever*" it might occur, as opposed to only at strategic places where the sensing devices are pre-located. The revolutionary advances in flexible sensing and distributed data processing permits us sensing in this truly distributed manner.

Sensors based on fiber optic cable functions make use of the following important features of the cable to sense the environment: (1) optical loss: intrinsic and extrinsic energy loss properties, (2) refractive index: index profile in radial direction and the reduction of index fluctuation along the axial direction; (3) shape: cross sectional shape and size, the surface finish and the fluctuation of the size along axial direction. Present fiber optic sensors mostly use energy loss principles (i.e., changes in optical power in linearly positioned wave-guides) for chemical

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detection. These can be limited for distributed applications if energy depletes over a short stretch of the fiber sensor, or frequent sensor points are needed at a prohibitively expensive cost. Other sensors use the changes in refractive index and/or cross sectional size of the fiber cable that change the light scattering property in optical fibers, known as Brillouin scattering (Horiguchi et al, 1995; Kee et al, 2000).Fiber optic sensing based on Brillouin scattering has been used successfully in civil infrastructure for health monitoring (Bao et al, 2001; Ohno et al, 2001). In this chapter a background on use of optical fibers for chemical sensing and new developments and proposed advancements are discussed.

2. Background

2.1. Overview of fiber optic sensors

In an optical fiber sensor a physical, chemical or biological variable can interact with the light and produce a change in one of their parameters. It is desirable to produce an optical signal related uniquely to the parameter of interest. These sensors use the optical fiber either as the sensing element (intrinsic sensors), or as a means of relaying signals from remote sensing area to the signal processor (extrinsic sensor), or both. Optical fiber sensors take advantage of the inherent fiber optic characteristics which include their lightweight, of very small size, passivity, low-power requirement, resistance to electromagnetic interference, environmental impact and corrosion, their bandwidth, and flexibility. They can be installed in areas normally inaccessible by conventional sensors, they can be interfaced with data communication systems and pose no risk of electric shock in live measurements. These attributes have allowed optical fiber sensors to displace traditional sensors for measurement and monitoring of rotation, acceleration, electric and magnetic field, temperature, pressure, acoustics, vibration, linear and angular position, strain, humidity, viscosity, pH, gas and chemical content among many others.

Use of Fiber Optic Sensors is a viable real-time data gathering approach by surface-adhering or embedding the fiber to a specimen under evaluation. The concept of embedding fiber-optic sensors into structures has generated a great deal of interests in aerospace engineering initially and more recently in civil engineering. There are several types of chemical sensing techniques based on optical waveguides (Ho et al, 2001). Among those are fiber Bragg gratings (FBG), which is marking of a fiber with a laser to create a local narrow band pass filter sensitive to environmental parameters (Guemes et al, 1998; Schulz et al., 1998). Optical time domain reflectometry (OTDR) consists of sending a powerful light pulse and observe modification in the reflected light due to local in homogeneties along the fiber. The pulse losses correspond to specific environmental interaction. The evanescent pulse technique is also based on OTDR, in which the fiber cladding is modified to interact with the environment and the pulse travels partially through the cladding. These sensors demand large optical power, due to the cumulative energy loss at the points of contact with the chemicals.

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Over the last decade, there has been rapid development in the area of smart sensor technologies, in particular using structurally integrated optical fiber to form the basis for smart structure technology. A variety of configurations have been developed for measurement of strains and deformations in structures, including localized-type such as fiber Bragg gratings and multiplexed long gauge interferometric sensors, and distributed sensing schemes including Stimulated Brillouin Scattering (SBS) or Brillouin Optical Time Domain Analysis (BOTDA) (Bao et al, 2001) and Brillouin Optical Time Domain Reflectometry (BOTDR) (Pamukcu et al, 2006; Anastasio et al, 2007).

Between different types of optical sensors reported, there are those based on sensitive coatings onto the fiber surface, Fabry-Perot interferometers, long-period fiber gratings (LPFG), LPFG with sensitive films, hetero-core devices, fiber Bragg gratings on doped fibers (i.e, Germanium doped). Fiber gratings are structures consisting of a periodic perturbation of the optical and/or geometrical properties of an optical fiber. Depending on the pitch of the perturbation, fiber gratings fall into two distinct categories: short period gratings, known as fiber Bragg gratings (FBGs) and, long period gratings (LPFGs). Stretching the fiber gratings causes a change in grating period, hence the wavelength of the reflected light. This makes the FBGs ideal for localized temperature and strain measurements. Unlike FBGs in which counter directional coupling occurs in the core, co-directional coupling occur in LPFGs between the core and cladding. This feature renders LPFGs sensitive not only to temperature and strain, but also to bending causing a curvature, to hydrostatic pressure, to torsion and to ambient refractive index changes. The closer the ambient refractive index to that of the cladding the stronger the sensitivity to refractive index changes. It is this high sensitivity that has piqued the interest in development of various types of refractive index-based LPFG sensors which constitute most of the chemical sensing applications (Orellana and Haigh, 2008; Kasik et al, 2010).

Point detection fiber optic sensors have been developed successfully for measurement of liquid levels, chemical species, drugs, environmental agents (such as pollutants and pesticides), biochemical reactions, and to monitor a wide variety of chemical processes (Wolfbeis, 2000). A fiber optic laser induced breakdown spectroscopy method was demonstrated in the field using a push-cone device, which is a single point, single time measurement technique. The most common configuration for optical pH sensors, and other environmental parameters, employs a fluorescence indicator (Lee et al, 2000). Among the different types of optical fiber devices used in pH sensing are, hetero-core fibers, U-bend fibers, fiber Bragg and long-period gratings, fibers and fiber tips with active doped cladding, among others (Kocincovaet al, 2007). Some of the substances that can be detected or identified using optical fiber sensors are volatile organic compounds (alcohols, formaldehydes, methane, ketones, CO_x, O_2, and H_2), some metallic ions like Ca, Al, Cu, Zn, Hg, V and Pb (Jeronimoet al, 2007; Wolfbeis, 2008).

Wide application of advanced chemical sensing in the environment may suffer from scaling issues. The real-world conditions often require self-referencing, spatially distributed, temporally continuous, and chemically selective sensors for monitoring regions spanning over long lengths or wide areas. When large area monitoring for chemical agent intrusion is required, use of currently available point sensors can be cost prohibitive. Other non-point, distributed

detection methods based on energy loss principles (Buerck et al, 2001) may also be inadequate when scaled to wide area monitoring due to extensive energy input requirements.

One of the unique features of the optical fiber technology is the possibility to construct distributed sensors, in which the measuring can be determined along a line of space with a given spatial resolution (Galindez-Jamioy et al, 2012) by, for example, Brillouin optical time domain analysis (BOTDA) (Cui et al., 2009, 2010 and 2011); an hetero-core LPFG sensors. In here, we examine current and proposed application of these techniques to spatially distributed, temporally continuous, and chemically selective sensing applications in soil and water environment. The premise of Brillouin technique goes back to 1920 when physicist Leon Brillouin first studied the diffusion of light by acoustic waves. The phenomenon he observed was a frequency change of scattered light. The first major papers related to distributed fiber optic sensor based on Brillouin were generated in mid-nineties (Bao, et al. 1995; Fellay et al, 1997). Current research on Brillouin sensing may be divided in three categories: photonics (the physics of Brillouin); data processing and post processing to improve signal to noise ratios, and applications of distributed sensing to civil infrastructure and environment.

2.2. Fundamentals of optical techniques

The interest on optical techniques to measure or detect chemical agents have been continuously extending and growing over the last forty years. Special attention has been focused on the development of optical sensor to detect heavy metals, due to the hazardous effects of these ions on the health of human beings and ecosystems. Optical methods have the advantage of being fast, simple, compact, portable, low-cost, with sensitivities and resolutions improved to detect in the picomolar range.

Combined with other technologies, like microfluidics systems, optical waveguides, or MEMs, optical methods are suitable for application where conventional electrodes cannot be used because of their large size or because of the risk of electrode shock during in vivo measurements. Due to their minute size; these optical microsystems are capable of gathering diverse data with a small amount of analyte. The diversification of optical techniques have made possible to construct novel sensing platforms to detect heavy metals in air, water or soil, food and beverages, or biological samples.

Optical sensors to detect heavy metals employ an optical transduction technique, i. e. an element that "translate" the chemical variable into an optical signal (intensity, wavelength, polarization or phase), to yield analyte information (McDonagh et al, 2008, Grattan and Meggitt, 1999). Optical chemical sensors can be categorized, according to the transduction technique, in direct sensors and reagent-mediated sensing systems. In direct sensors the element of interest is detected directly via an optical property of the sample such as scattering or florescence, for example.

However, most heavy metals optical sensor uses an intermediate agent. Most of the optical chemical techniques to detect heavy metals are based on optical absorption, fluorescence, Raman spectroscopy, or surface plasmon resonance, whereby the perturbed signal is related to the reaction of the intermediate agent under the presence of a specific heavy metal. In

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general, all these techniques involves the interaction of an incident beam over an analyte or indicator element yielding transmitted, reflected or fluorescent signal. A schematic representation of the spectroscopic principle, the working mechanism of an optical sensor is shown in Figure 1.

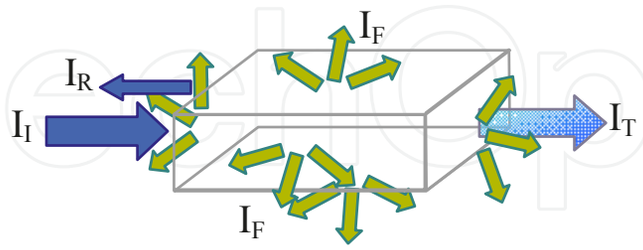


Figure 1. Representation of the optical signals in an optical chemical sensor. The incident beam I_I interacts with the heavy metal sensitive layer and depending on the optical properties of the sample one of the three signals (transmitted I_T, reflected I_R, and generated by fluorescence or scattering I_F) will be produced and will give information about the type and concentration of heavy metal present on the sample.

2.2.1. Absorbance-based techniques

Among the optical chemical techniques, the simplest to implement is that based on the measurement of light absorbed by a sensitive heavy metal layer. Absorption in a gas or liquid, where it is assumed that each single molecules equally contributes to the total light absorbed, may be characterized by a Beer-Lambert law, or simply the Beer law,

$$I_T = I_I 10^{-\varepsilon C d} \tag{1}$$

where I_T and I_I represents the intensity of the transmitted and incident beam, ε is the molar absorptivity ($Lmol^{-1}$ cm), and C is the concentration (mol L^{-1}) of the absorbing species and d is the absorption path length (cm). In the case of a solid, absorbing and homogeneous medium, the transmitted signal is calculated using the Lambert Bouguer law, expressed as $I_T = I_I e^{-\alpha x}$, where x is the thickness of the medium and α is the extinction coefficient. The Beer law can also be expressed in terms of the absorbance (or optical density) A:

$$A = \log_{10}\left(\frac{I_I}{I_T}\right) = \varepsilon C d \tag{2}$$

There exists a linear relation between the absorbance and the concentration of the element to be measured. However, in order to observe the linear dependence of absorbance on concentration, the incident beam should be ideally monochromatic. In the case that a wide broadband light source is used, the contribution of all wavelengths must be considered, in such cases the equation (2) becomes:

$$\bar{A} = \log_{10}\left(\frac{\int I_I(\lambda)d\lambda}{\int I_T(\lambda)d\lambda}\right) \tag{3}$$

Also the presence of highly absorbing or highly scattering media should produce a deviation from perfect Beer law behavior. In the case that more than one absorbing material is present the absorbance contribution of each species must be considered. In most of the absorbance-based heavy metals sensors an intermediate agent, an optical film that changes its absorbance according to the concentration of a specific heavy metal, is used (Antico et al, 1999;Guo et al, 2006).

A special case of the absorption-based sensors are those schemes where materials that change their color under the presence of a specific heavy metal are used (Balaji et al, 2006; Prabhakaran et al, 2007). The reaction of the sensitive components to the concentration of a specific ion produces a photochromic reaction that can be observed with a naked eye. Such materials are often in solution, but for sensing the most attractive are those that can be deposited as thin films over a substrate. The instrumentation of absorption-based sensors is the simpler of the optical heavy metal techniques, since it can be implemented with a monochromatic light source and a photodetector. This also makes this technique very susceptible to be implemented in microscopic opto-fluidic configurations that could diversify the technique.

2.2.2. Reflectance-based techniques

It is well-known that chemical reactions could lead to changes in the complex refractive index of a substance; this fact has been impulse researchers to design and fabricate materials that react with heavy metals that can be used as transducers. When these materials, commonly in the form of a thin layer, are illuminated with an appropriated light the signal will be partially or totally reflected. However, this reflectance will change when the layer is in contact with a specific metal that it reacts with. If the refractive index of the layer is purely real, the changes in the reflected signal can be estimated by using the Fresnel formulae.

However, in most cases the optical response of these materials under the presence of heavy metals are more complex and involve a change in the real and imaginary parts of the refractive index, that produce changes in reflectivity and absorbance. Also, there is a contribution of scattered light. So, the reflected signal is composed of light from different sources, however, also in this complex response the signal reflected is used to deduce, directly or indirectly, the concentration C of the heavy metals.

The reflected-based techniques are specially used in optical fiber schemes since the set-up is very simple to implement (Yusofand Ahmad, 2003, Guillemain et al, 2009). The material sensitive to the heavy metals are directly deposited over the fiber tip or in a substrate that will be illuminated by an optical fiber. The reflected signal is usually collected by the same fiber, but frequently another fiber or fibers are used to collect it. The reflected signal propagates along the fiber to the detector, where it is analyzed in order to determine the heavy metal present and their concentration (Figure 2).

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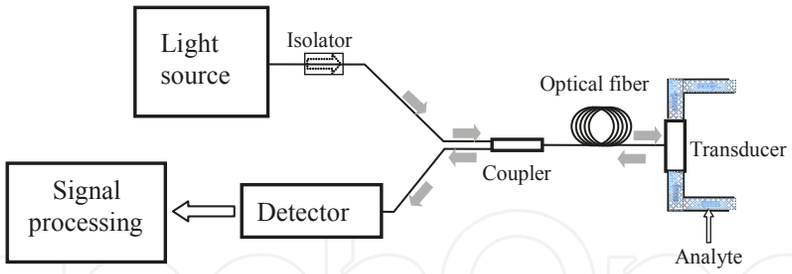


Figure 2. Diagram of a reflectance-based optical chemical sensor based on optical fibers.

2.2.3. Fluorescence-based techniques

Some materials have the property of being fluorescent when they are illuminated with a light source of appropriated wavelength. The fluorescence is the optical radiation generated when electrons of an atom or molecule return from the excited to the ground state after absorption of a photon from an excitation light source. In general the energy of the excited photon is lower than the absorbed one so the wavelength of the fluorescence signal is longer than that of the excitation.

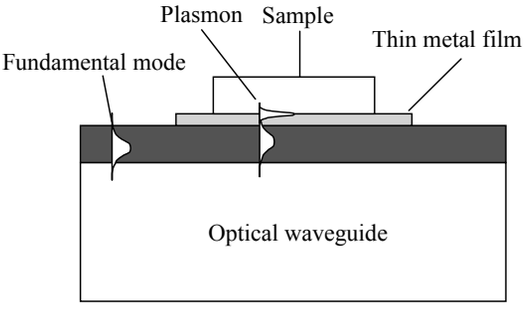
The intensity of the fluorescent signal (I_F) is proportional to the intensity of light absorbed by the sample (I_I-I_T), therefore it is possible to establish a direct relation between the intensity of the fluorescent signal and the concentration of an absorbing material. This feature is very important for sensing since intensity of the fluorescence increases as the concentration of the absorbing species augments. Although, we have just made reference to the fluorescence intensity, for sensing, the decay time of the fluorescence signal is more frequently used because this parameter is less sensitive to source fluctuations, interference from ambient light or drift due to aging of detector. It is possible to design and fabricate a fluorescent material sensitive to a specific heavy metal. Thus, the intensity, wavelength and life time of the fluorescent signal will change under the presence of this metal. Fluorescence-based techniques are the most used to detect the presence of heavy metals due to its extraordinary sensibility (Mayra et al., 2008;Achatz et al, 2011, Aksuner, 2011).

2.2.4. Surface plasmon resonance-based techniques

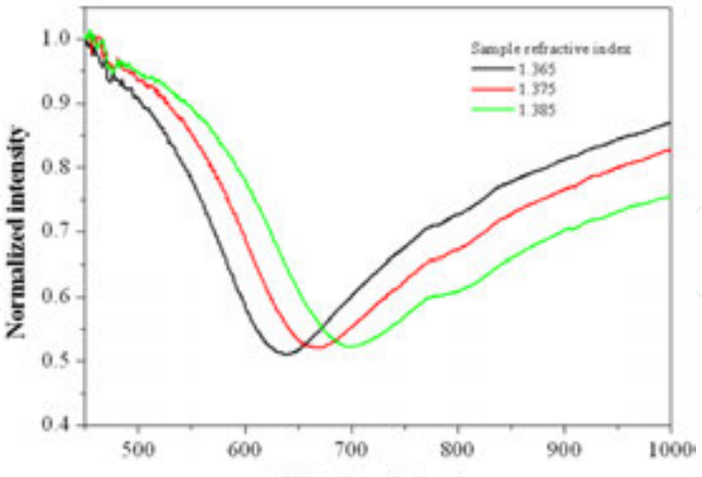
The most popular label-free refractometric technique is the Surface Plasmon Resonance (SPR), since it allows the direct observation of chemical reactions in real time without the use of markers or labels. SPR is a quantum optical-electrical phenomenon produced by the interaction of light with a metal surface. Actually, the surface plasmon is a charge density oscillation that exists at a metal-dielectric interface. The plasmon propagates in a direction parallel to the metal-dielectric interface in the boundary of the metal and the external medium (Figure 3).

These oscillations are very sensitive to any change in the optical refractive index of the material at the boundary. The optical excitation of plasmon can be achieved in a three-layer system consisting of a thin metal film sandwiched between two isolators of different dielectric constant

(Maier, 2007), where the phase-matching condition between the optical and plasmon wave vector is fulfilled. In the optical domain, the surface plasmon excitation will be observed as an intensity transmission loss at a specific wavelength. The wavelength of the dip depends on the refractive index of the two dielectrics and the thin metal film, and the propagation constant of the optical waveguide. There are three common method to excite surface plasmon, using a prism coupler and the attenuated total reflection, a periodic grating, and an optical waveguide planar (Figure 3A) or cylindrical. The prism coupler technique is the most popular since exhibits a good sensitivity, stability, and reproducibility for the measurement of heavy metals (Forzani et al, 2007; Lin et al, 2009; Abdi et al, 2011; Fen et al, 2012 and 2013; Fen and Yunus, 2013). For heavy metal detection a sensitive thin film layer is deposited over the thin metal film, so when the target heavy metal interacts with the layer a refractive index change is produced. The surface plasmon conditions changes and the peak wavelength shifts as can be seen in Figure 3B. SPR is the most sensitive refractometric method, with a theoretical resolution of $1x10^{-7}$, so it is possible to detect very small traces of heavy metals.



A



B

Figure 3. (A) A schematic representation of the surface plasmon excitation in a dielectric planar waveguide coupler configuration. (B) Optical transmission spectra of an hetero-core optical fiber coated with a 20 nm thin gold film when the fiber is immersed in a liquid with a refractive index of 1.365, 1.375, and 1.385, black, red and green line respectively.

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2.3. FUNDAMENTALS OF BOTDA AND LPFG BASED SENSING.

Figure 4, 5and 6show the stimulated Brillouin scattering based BOTDA photonics configuration and the principle of measurement used at Lehigh University Geo-sensing laboratory, respectively (Texier et al, 2005; Pamukcu et al, 2006; Turel and Pamukcu, 2006; Anastasio et al, 2007). Brillouin is a nonlinear effect, in which light is scattered at well-defined points along the fiber where the acoustic properties of the fiber are locally modified by the environment. The stimulated Brillouin scattering (SBS) it is an acoustic – optical process which is useful for distributed measurements of a probe beam by the SBS interaction with a counter-propagating nanosecond pump pulse. In the SBS technique, as in a null detector, the pump and probe are initially de-tuned by a Δ(frequency) that is slightly greater than the Brillouin frequency. Therefore, in unstressed fiber, the base line remains flat resulting in a self-

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The Brillouin line being intrinsically narrow (~20 - 50 MHz), the initial de-tuning can be quite small so that the amount of strain required to generate a signal is also quite small (0.001 %), allowing for higher resolution and sensitivity of the sensor compared to other fiber-based measurement techniques. When SBS based sensors are used for environmental sensing the fiber is hitched or bonded with selective polymer transducers that are mass detectors in direct contact with the surrounding medium. The polymer reacts to the surrounding (i.e. moisture, pH, target chemical) by selectively absorbing the target compound and it swells. Localized swelling of the bonded or hitched polymer produces tangential, axial or radial stresses on the fiber depending on the physical coupling. These stresses result in axial straining of the fiber and a measurable change in its local acoustic properties, hence a Brillouin scatter of the transmitted light. The location of the generated signal is determined by time domain reflectometry.

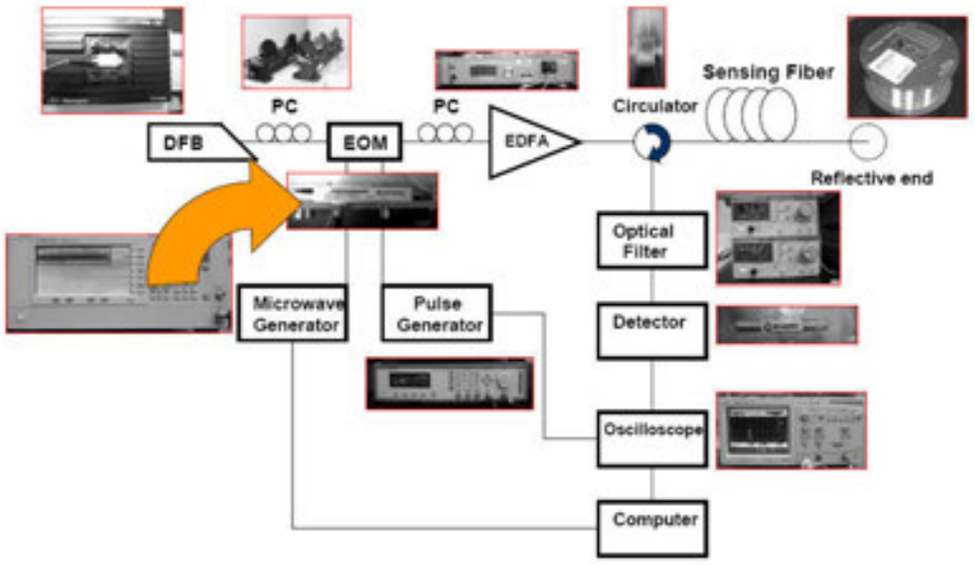


Figure 4. SBS based BOTDR photonics set up at Lehigh Geo-Sensing Laboratory.

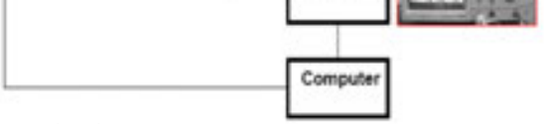


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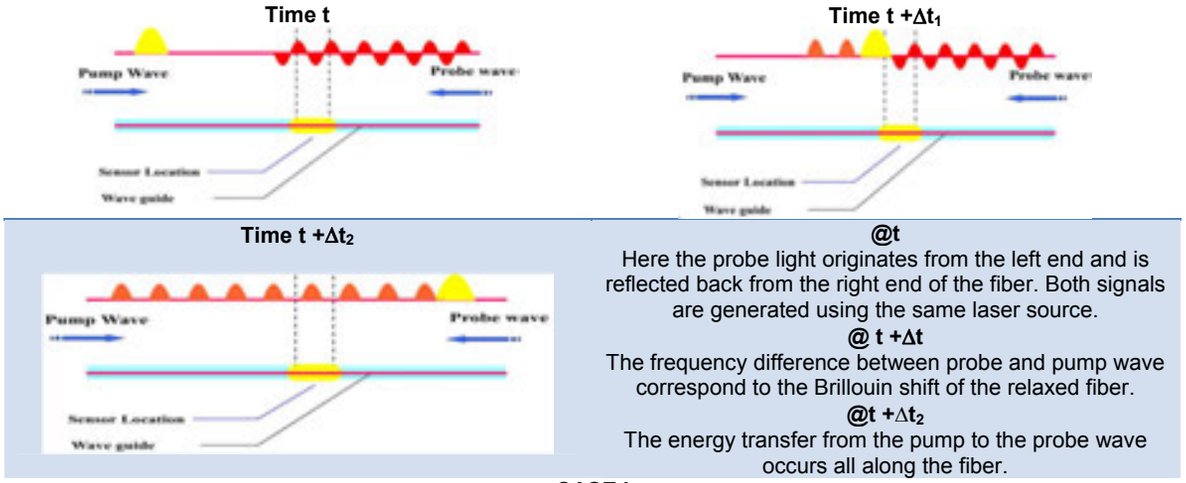


Figure 5. Measurement principles of SBS based sensing: case I.

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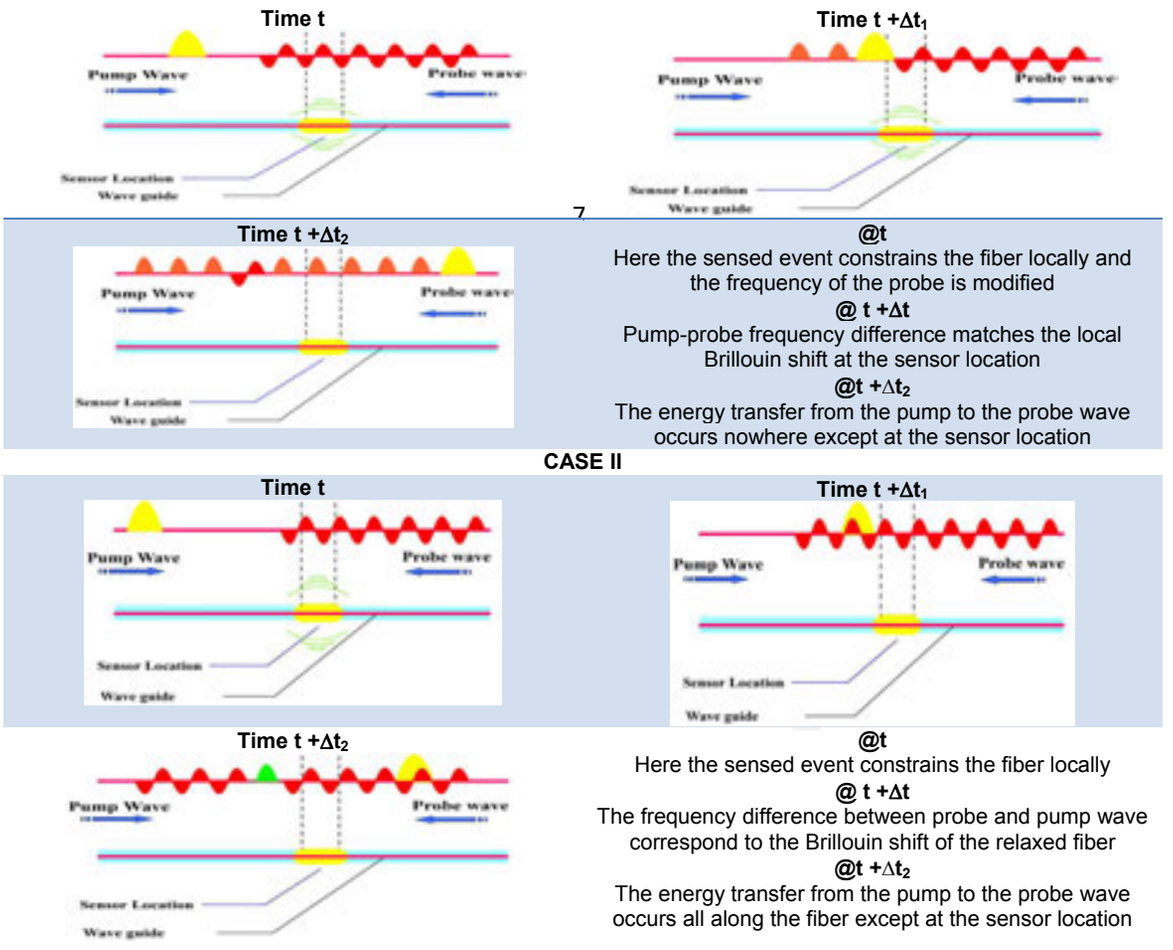


Figure 6. Measurement principles of SBS based sensing: case II and III.

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In the case of LPFG`s the environmental changes produce a spectral shifts, that required a sophisticate or a complicate equipment. These devices are very sensitive to temperature changes so to measure another different parameter it is necessary to make the corresponding compensation. One alternative to avoid these difficulties are hetero-core fibers. These devices are constructed by changing the diameter of the core in a small length (mm) in a transmission line (Figure 5 and 6), which causes the optical wave to expand within the cladding in the single-mode region of the hetero-core, thus the evanescent field can easily interact with the external medium.

Owing to the core diameter mismatch, some of the light is guided by the cladding of the SM fiber (Figure 7). This makes the transmission of the device dependent on the refractive index of the external medium. The sensor exhibits maximum transmission changes when the index of the sample medium approaches that of the SM fiber cladding. The device can operate at different wavelengths as well as when coated with thick films made of variable index materials. Moreover, standard emitters, fibers, detectors, etc., are needed to fabricate the sensor, which makes it attractive for diverse applications (Villatoro and Monzon-Hernandez, 2006).

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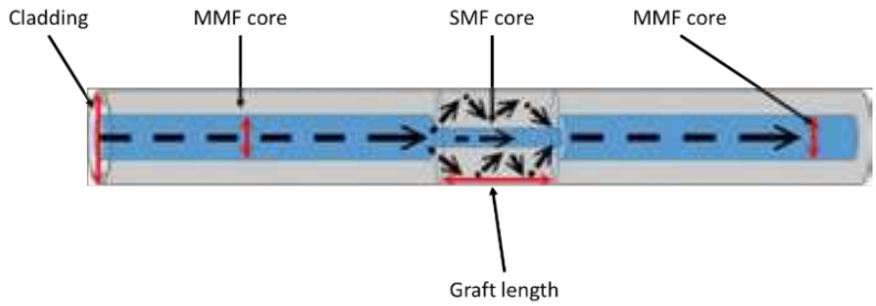


Figure 7. Schematic representation of the hetero-core fiber structure. A piece of single-mode fiber (SMF) of length L is inserted between two multimode fibers (MMF). Cladding diameter of both fibers is 125 μm but the core diameters are different.

3. Investigation

3.1. BOTDA/BOTDR applications and proposed sensor configurations

The usefulness of SBS for sensing is general: any change in external conditions, that affects the acoustic properties of the optical fiber, can in principle be detected. This is true of direct temperature and pressure changes, but can also be true of changes in chemical environment that can be made to result in temperature and pressure changes. An SBS based BOTDR sensing system was used to detect water content changes in soil. Water transducers (hydrophilic polymers) were tested to correlate Brillouin strain response to the water content of the surrounding soil environment. In these experiments, the optical fiber was wound and secured about discretely placed discs (2 cm length x 5 cm diameter) of AEP60 hydrophilic polymer (Figure 8A), stringed along 100-m fiber continuous optical fiber. The diameter of the polymer

3. INVESTIGATION.

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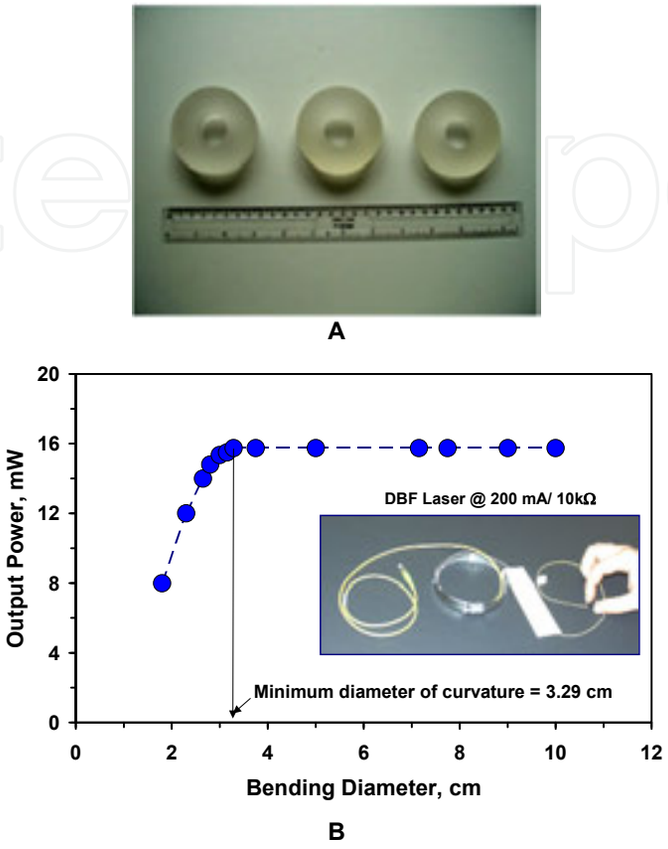


Figure 8. A photograph of the AEP60 hydrogel polymer discs used in sensor (A); assembly and test results for minimum fiber bending radius assessment (B).

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The optical fibre at the inlet and outlet of the string of four transducers were spliced to spools of fibre on each end, and connected to the photonic set-up. Each water transducer was then embedded in a wet clay sample of predetermined water content (5, 10, 20 and 30 % by dry weight of clay), as shown in the inset sketch of Figure 9B.

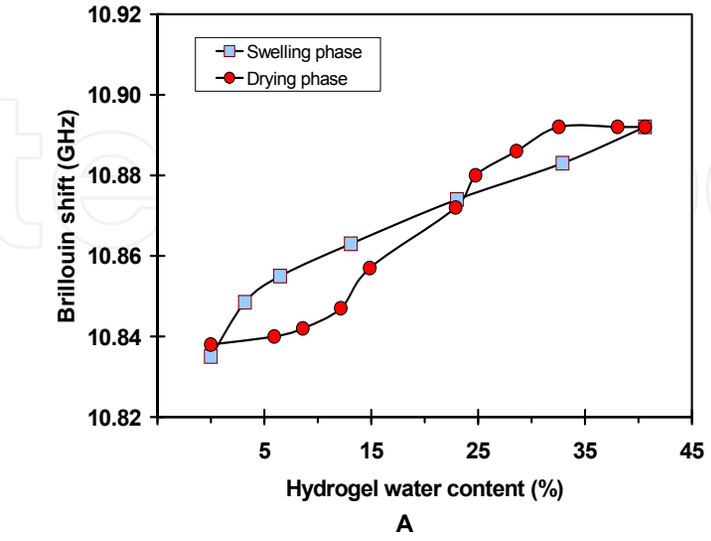
The clay samples were packed in equal volume, watertight, cylindrical cells of 14-cm diameter and 28-cm height. The experiments were conducted in a temperature-controlled environment, at 25°C so that Brillouin scattering measurements were not influenced by thermal expansion or contraction of the fibre. The Brillouin shift was measured with 5 to 20 minute intervals up to the maximum observable swelling. When no significant change in Brillouin shift was recorded for three consecutive measurements, the transducers were removed from the soil chambers and left for open air-drying.

The Brillouin shift measurements were recorded with 5 to 20 minute intervals until the drying phase was completed. Since Brillouin readings could be recorded for strains as low as 10, very small volume change due to water absorption could be detected in a few minutes. Figure 9B

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Figure 9A shows the calibration of Brillouin shift versus water content gain of the hydrogel disc coupled to the optical fiber. The hysteresis between the swelling and drying cycles is attributed to the diffusion trends affected by the geometry of the hydrogel transducers. The ends of the discs were exposed to diffusion as well as the cylindrical surfaces which resulted in uneven strain distribution in the fiber.

shows the time rate of Brillouin signal changes during the hydrogel swelling and drying cycles of the 4-different water content clay hosts.



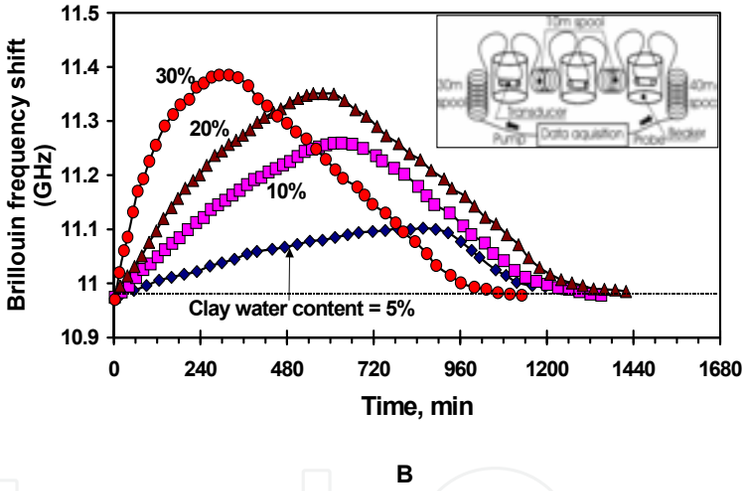


Figure 9. (A) Calibration of Brillouin Shift of fiber versus the water content by dry weight of the hydrogel disc. (B) Brillouin signal shift as a function of swelling/shrinkage time and clay water content (*Inset* – sketch of experimental set up).

Figure 9. (A) Calibration of Brillouin Shift of fiber versus the water content by dry weight of the hydrogel disc. (B) Brillouin signal shift as a function of swelling/shrinkage time and clay water (B) Brillouin signal shifts as a function of swelling/shrinkage time and clay water content (*Inset* – sketch of experimental set up).

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In the experiments, the clay samples were packed in equal volume, water tight, cylindrical cells of 4 cm diameter and 28 cm height. The clay samples were packed to equal volume densities and were hydrated to a uniform water content. The experiments were conducted in a temperature-controlled environment at 25°C so that Brillouin scattering measurements were not influenced by thermal expansion or contraction of the fibre. The Brillouin shift was measured with 5 to 20 minute intervals up to the maximum observable swelling. When no significant change in Brillouin shift was recorded for three consecutive measurements, the transducers were removed from the soil chambers and left for open air-drying.

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The Brillouin shift measurements were recorded with 5 to 20 minute intervals until the drying phase was completed. Since Brillouin readings could be recorded for strains as low as 10με, very small volume change due to water absorption could be detected in a few minutes. Figure 9B shows the time rate of Brillouin signal changes during the hydrogel swelling and drying cycles of the 4-different water content clay hosts.

In the experiments described above, the AEP60 polymer used would typically expand from 38% to 400% over dry volume when exposed to water. They are non-toxic and are manufactured in medical grades, approved for use in human wound care applications. This group of polymers does not swell in hydrocarbons and chlorinated solvents and has high thermal resistance. They are cross-linked to give them mechanical stability and accurate expansion characteristics. The water absorption and expansion factor can be accurately pre-defined at the formulation stage. Full expansion is reproducible over many wetting and drying cycles and is consistent over a wide range of pH and dissolved solid concentrations. A different integration of optical fiber and polymer transducer was used to improve the polymer response kinetics as shown in Figure 10. In this design, the polymer was reduced to smaller size discrete sleeves as (1cm length x 0.3 cm diameter) that were bonded over the optical fiber. The bonding adhesive used was Locktite 414, a super bonding, quick drying adhesive containing cyanoacrylate and is intended for plastics and vinyl. The Locktite 414 was applied to each end of the polymer sleeve also.

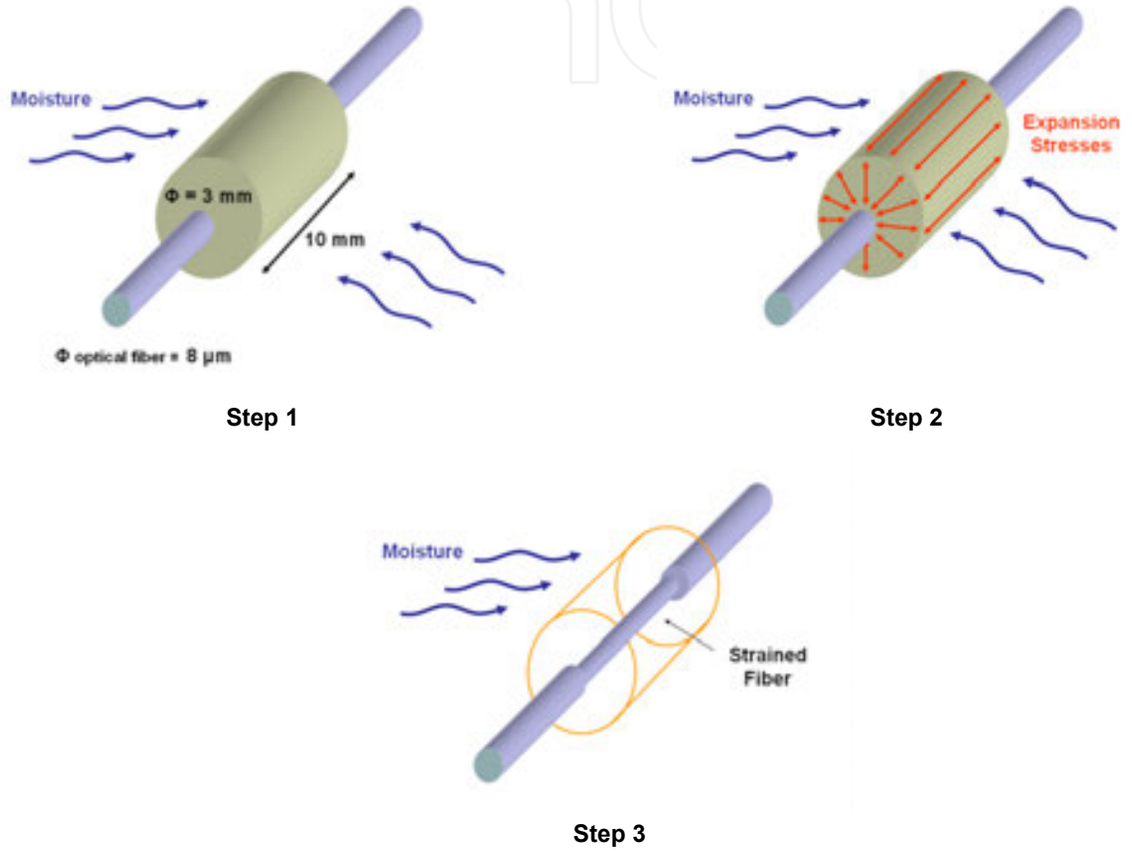


Figure 10. The working principle of the integrated sensor. Step 1 - Solution sorbed by the chemical selective polymer sleeve bonded onto the fiberoptic cable. Step 2 – The selective polymer swell upon encountering the target compound or ion in the solution. Step 3 – The swelling of the bonded polymer sleeve induces a "tangential pull" or "axial strain" on to the fiber locally.

The reduced size was anticipated to improve the swelling kinetics and alleviate the hysteresis affects observed in the previous configuration. The working principle of the integrated sensor is also depicted in Figure 10, where first the influx of the target substance (e.g. water) into the polymer transducer causes swelling of the bonded polymer. The swelling causes the bonding interface to strain and cause the fiber elongate in tangential pull. The fiber strain can then be recorded with location and amplitude, as shown in Figure 11, indicating where along the fiber line the influx of the target substance had occurred, and also the calibrated quantity of the substance based on the degree of swelling of the polymer, respectively.

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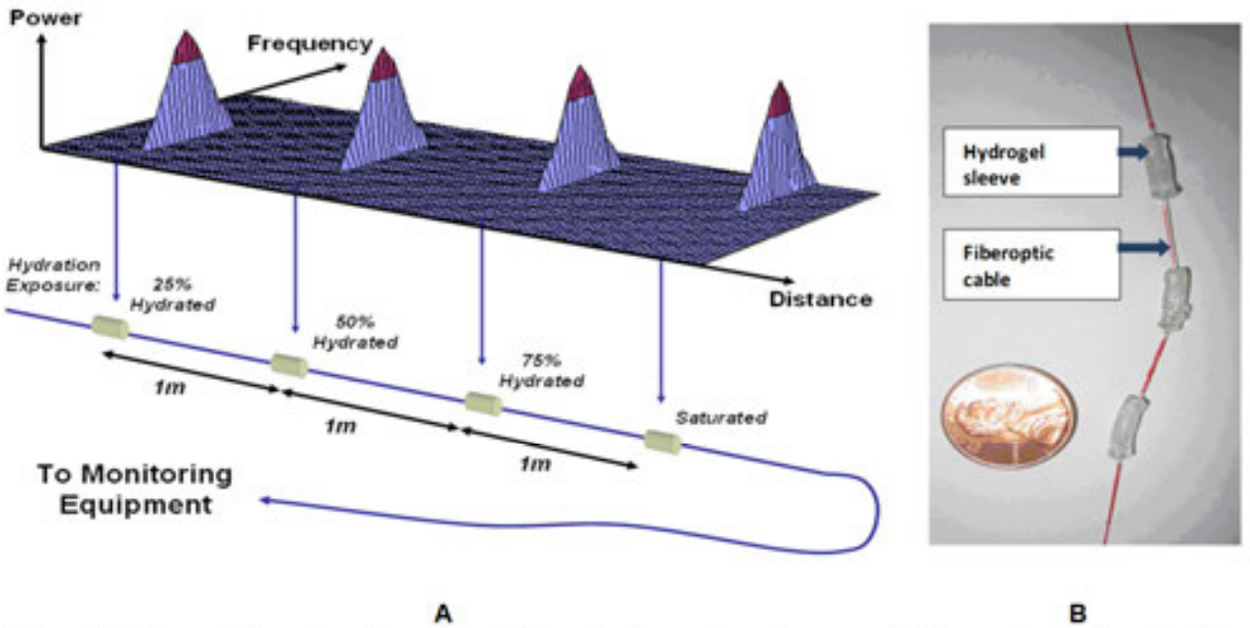


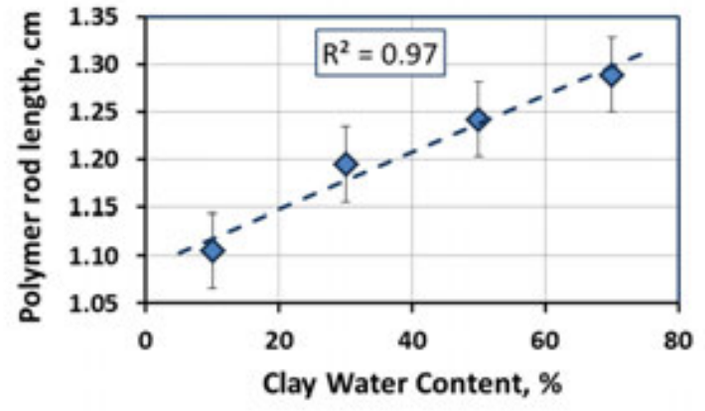
Figure 11. The operation schematic and the photograph of a spent water sensor: (A) Conceptual schematic of the integrated sensor assembly and its working principle as a distributed water sensor. (B) A laboratory prototype of the integrated water sensor.

Figure 11. The operation schematic and the photograph of a spent water sensor. (A) Conceptual schematic of the integrated sensor assembly and its working principle as a distributed water sensor. (B) A laboratory prototype of the integrated water sensor.

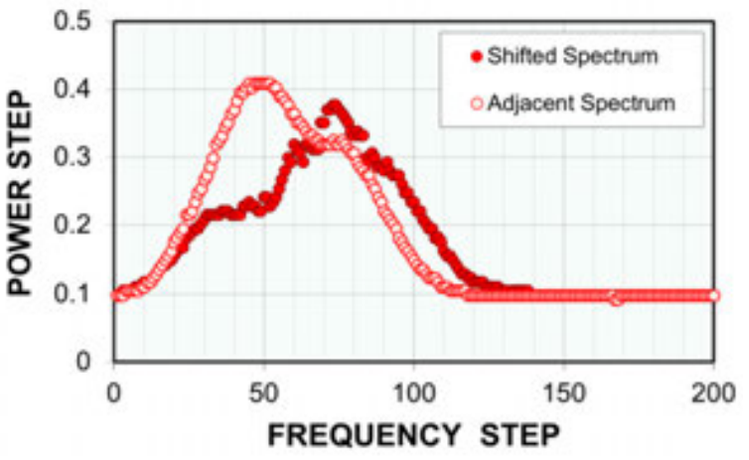
Repeated swelling and shrinkage tests of the polymer sleeve component of the integrated water sensor showed hysteresis of length and diameter change. Both the length and diameter of the of the polymer sleeve expanded by 35% (~ 0.35 cm and ~0.1 cm, respectively) after being soaked in water for three days. The majority of this expansion occurred during the first 12 hours of soaking. Increasing with every cycle, the final dry length of the polymer was greater than the original by ~ 0.025 cm (~2.5%).As more cycles were completed, the diameter increased to its maximum faster, but the value of this maximum decreased. The final diameter of the polymer sleeve was fairly constant for each cycle, slightly less than the original by ~ 0.0005 cm (~0.2%).

The magnitude and rate of swelling correlated directly with the initial water content when the polymer sleeves were embedded in test clay specimens of different water contents. Once again the full swelling occurred between 8 to 12 h when the sleeves were embedded in wet clay. Figure 12A shows that the polymer linear extension and clay water content relation was fairly linear. The linear relation is desirable for robust calibration. Figure 12B shows the dimensionless frequency shift response of the integrated water sensor to clay water content increase. The figure plots two spectrums, the shift spectrum at the location of the expanded polymer and a spectrum near the polymer location that does not undergo the swelling stress.

The actual Brillouin frequency shift was measured 0.0432 GHz corresponding to axial strain of 0.098% for the fiber. The actual elongation of the polymer rod was 3 mm, which fully transferred to the fiber would have corresponded to an average strain of 0.14% for the fiber over the 12.6 ns pulse. This meant that about 70 percent of the axial tug generated by the swelling of polymer was transferred to the fiber. The other 30 percent can be attributed to slippage across the length of the bond between the fiber and the polymer sleeve or other process related inefficiencies.



A



B

Figure 12. (A) Variation of embedded AEP60 polymer sleeve length vs clay w/c in swelling behavior. (B) Shifted frequency spectra for integrated sensor under swelling stresses with increased water.

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These test results demonstrated the viability of integration of optical fiber with reactive polymer as a BOTDR based sensor. Yet, the slow kinetics of the response (~12 hr for full swelling in case of water) rendered the prototype assembly limited for quick detection and measurement purposes. Hence a new polymer and fiber-optic cable configuration is proposed where a thin layer (e.g. on the order of few hundred μm) of the reactive polymer is brushed and bonded onto the fiber-optic cable. Figure 13 presents variations of the conceptual sensor where the reactive polymer coat is continuous. The working principle of this new configuration is similar to the previous ones described, all based on BOTDR, with the exception that the continuous coating of a thin layer reactive polymer is anticipated to provide a truly distributed and fast detection mechanism.

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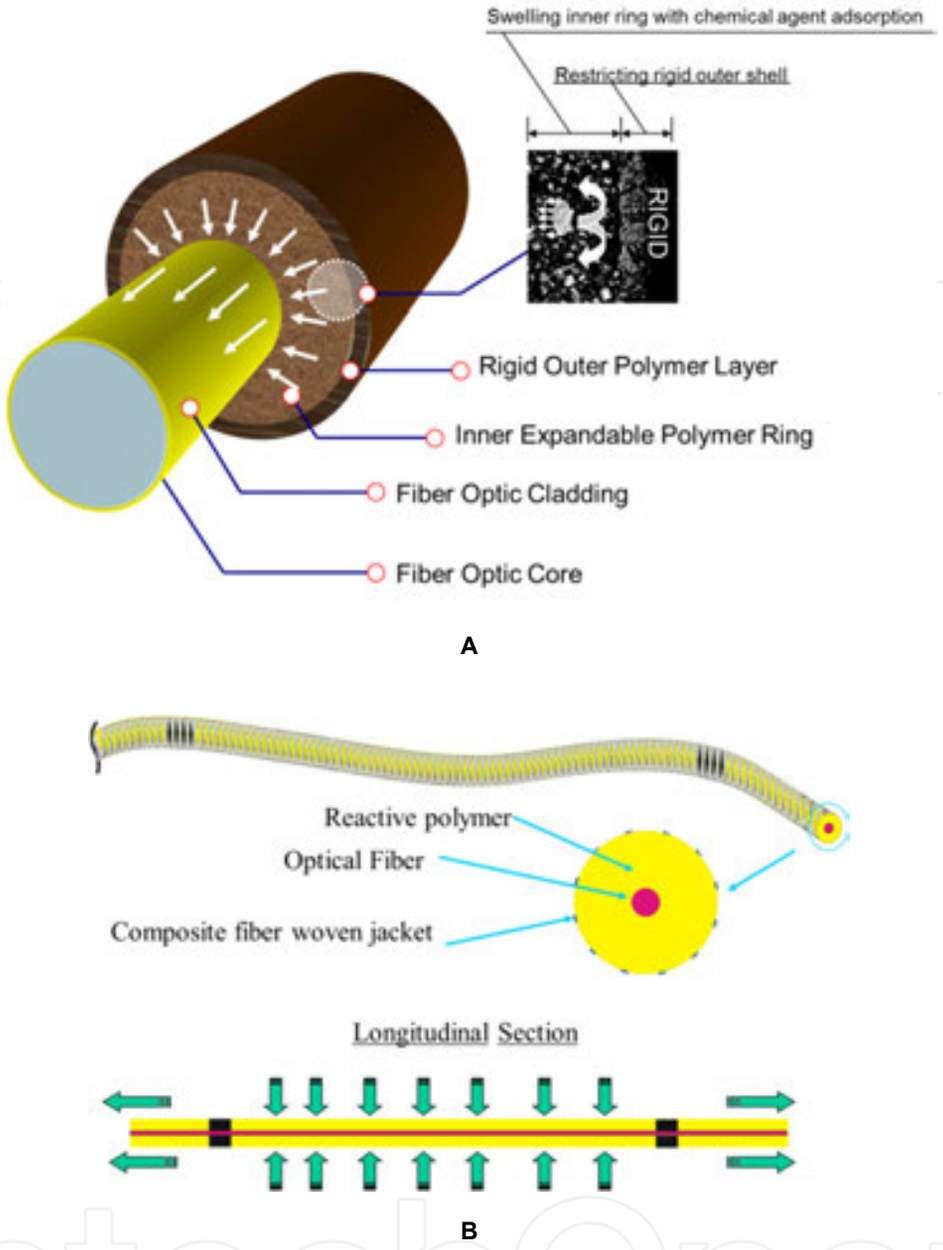


Figure 13. Advanced integrated chemical sensors based on BOTDR/BOTDA: (A) Cross-section of integrated sensor with core/shell polymer layers; (B) Working principal of an integrated sensor with polymer/jacket combination.

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3.2. Reactive polymers principles used as sensors

These test results demonstrated the viability of integration of optical fiber with reactive polymer as a BOTDR based sensor. Yet, the slow kinetics of the response (~12 hrs for full swelling in case of water) rendered the prototype assembly implied for quick detection and measurement purposes. Hence a new polymer and fiber optic cable configuration is proposed where a thin layer (e.g. on the order of few hundred um) of the reactive polymer is brushed and bonded onto the fiber-optic cable. Figure 13 presents variations of the conceptual sensor where the reactive polymer coat is continuous. The working principle of this new configuration is similar to the previous ones described, all based on BOTDR, with the exception that the continuous coating of a thin layer reactive polymer is anticipated to provide a truly distributed and fast detection mechanism.

Point detection fiber optic sensors have been developed for measurement of liquid levels, chemical species (inorganic and organic), drugs, environmental agents (such as pollutants and pesticides), biochemical reactions, and to monitor a wide variety of various chemical processes (Wolfbeis, 2000). One of the major components of a sensor system is the sensing or recognition element. Polymers have often been utilized as a chemical sensing material. The interaction of an analyte with the polymer coating is of prime importance. A signal needs to be generated once this interaction occurs, and much work has been carried out to understand the interaction

of the polymer coating with the analyte molecules, especially in terms of the diffusion behavior of the analyte through the polymer coating to the actual sensor itself and its subsequent enrichment within the polymeric coating layer (Philips, et al, 2003).

The integrated chemical sensor based on BOTDR discussed in here is a single SBS (Stimulated Brillouin Scattering) sensing optical fiber bonded with such a polymer, which swells selectively in the presence of a target chemical. The polymer coat is cross-linked to swell in a preferential direction. During swelling, the bonded polymer coat exerts a radial or tangential force at the polymer-fiber interface, hence an axial strain on the fiber. The SBS signals are generated along the fiber at the discrete points of chemical contact triggered by polymer swelling, hence the local axial strains in the fiber. Consequently, the location of the target chemical can be detected simply by linear positioning of the SBS signals over the entire length of the cable. Because the detection is based on local physical changes in the fiber and not on loss of transmitted light, widely distributed sensing is possible without high power requirements. The specific detection and measurement components of the integrated sensor described above include, a core/shell type (multi-layer) polymer coating, and an inner fiber optic cable core, or a rigid woven jacket conceptualized in Figure 13.

In this conceptual design, the outer cross-linked polymer coating (shell) serves as a rigid, high permeability filter and confinement to the inner polymer (core). The core is a flexible, chemically selective polymer, preferably with rapid mass sorption kinetics. While the highly networked rigid polymer shell confines and directs the cores welling toward the fiber optic cable, the selective detection of chemicals is based on the thermodynamics and kinetics of chemical sorption and swelling of the core polymer layer. A volume change or "swelling" occurs in the inner flexible polymer layer as a result of mass sorption of the surrounding analyte. Solute/solvent sorption interrupts the intermolecular forces between individual chains of a lightly cross-linked or a linear polymer adjacent to the glass fiber, resulting in swelling forces. The outer, permeable but rigid polymer layer comprised of highly networked cross-linked chains help confine the volume change tendency and direct part of the swelling forces inward (radially and/or longitudinally) thus creating a hoop or a tangential stress on the fiber at the polymer interface. This "pinch" or tug" of the fiber cause changes in the elastic and refractive properties of the fiber locally, generating a shift in its original Brillouin frequency at that local. Comparing the new frequency to the original, it is then possible to quantify the change in terms of the swelling forces and the quantity of the absorbed substance.

A multi-chemical sensor can be developed by bundling polymer-coated fibers of different functions and sensitivities. The entire sensor assembly can be several tens of kilometers of optical fiber hosting several 100 measurement locations on the same line, each at a minimum spatial resolution of 1-meter. The photonics assembly connected to one end of the fiber allows fast detection of discrete sensing locations rendering the entire assembly a multiplexed network of many point sensors on the same transmittal line. Hence, the fiber line coupled with the stringed transducers can be embedded linearly or laced into a host medium (i.e. water pipeline, paved surfaces, porous media such as soil or concrete) to detect target chemical(s) online over large distances, areas or spaces by linear positioning of the fiber.

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3.2.1. Reactive polymers

The molecularly imprinted polymers are often used to improve selectivity (Wolfbeis, 2000; Philips et al, 2003). The incorporation of desired functional monomers into the polymer structure further enhances the selectivity to a given analyte. These polymers are cross-linked and prepared by free radical polymerization processes such as solution or dispersion polymerization with acrylic or vinyl monomers. Polyelectrolyte gels are charged cross-linked three-dimensional networks of monomers that possess high swelling capability due to solvent sorption. The amount of swelling is known to be a string function of pressure, temperature, ion concentrations and pH changes (Siegel, 1993; Siegel et al, 1998; Matsuo and Tanaka, 1988). Their swelling and kinetics depend on parameters such as the degree of cross-linking (Skouri et al, 1995), external salt molarity (Yin et. al, 1992), and the degree of gel ionization rule (Katchalsky and Michaeli, 1995; Yin et al, 1992).

An emulsion or miniemulsion polymerization approach can be utilized to prepare film-forming polymer latexes with desired functional moieties to be used to coat optical fibers. The base latex polymer may be based on acrylic (e.g., *n*-butyl acrylate, n-butyl methacrylate) or styrene/acrylic film-forming compositions (i.e., with glass transition temperatures (T_g) of room temperature or lower). These latexes are prepared by conventional emulsion polymerization or by a miniemulsion polymerization process in the case where monomers with very low water solubility are used. In the miniemulsion polymerization process, the monomer would be emulsified in the presence of an aqueous surfactant (such as sodium lauryl sulfate) / costabilizer (e.g., hexadecane dissolved in the (co)monomer mixture) combination using a high shear device to form miniemulsion droplets which could then be polymerized in the presence of a free radical such as potassium persulfate.

The polymer would also be crosslinked to varying extents using crosslinking monomers such as ethylene glycol dimethacrylate, divinylbenzene, or bisacrylamide. In addition, functional monomers can be copolymerized along with the base acrylic or styrene/acrylic monomers. One type of monomer is a carboxylic acid such as methacrylic acid (MAA), which copolymerizes well with the base monomers. At high concentrations, this latex could function as an alkali-swellable latex whereby the latex particle size, and coating swellability, would increase dramatically upon neutralization in aqueous solutions of high pH (e.g. > 10) which would trigger a sensor response. N-methylol acrylamide (NMA) may also be incorporated into the base copolymer composition to obtain a crosslinked polymer, which can also act as a hydrogel, which could also swell when exposed to water. In addition, the monomer, N-(isopropylacrylamide) (NIPAM) will also be utilized for forming hydrogel particles which can swell when exposed to water. Incorporating NIPAM into a polymer composition would also lead to the formation of a thermosensitive polymer coating since poly(NIPAM) exhibits a strong phase transition above 32°C. It is also possible to copolymerize a alkoxysilane-containing monomer with the acrylic or styrene-acrylic monomers via miniemulsion polymerization to enhance the compatibility of the polymer coating with the glass optical fiber.

3.2.2. Bonding/lamination

The extent of bonding of the polymer coating to the glass optical fibers is critical. The optical fibers can either be coated with the manufacturer's cladding removed or in place. Preliminary experiments have shown that it is difficult to coat the uncoated glass fibers. These fibers are brittle without the manufacturer's cladding in place; the composition of which is unknown. The fiber can be passed through a coagulant bath prior to its immersion in the latex bath. Similar to dip coating, which has been utilized in preliminary coating experiments, the latex will coagulate onto the glass fiber. The surface of the fiber needs to be made hydrophilic for this process. This can be achieved by either physical adsorption of nonionic water-soluble polymer such as poly(vinyl alcohol) (PVOH) or by corona treatment of the fiber surface. In addition, the polymer processing techniques used in wire coating applications can also be applied to the case of the optical fibers. Important coating parameters would include the solids content of the latex (a high solids content is needed to control the rheology of the dispersion to be coated; a reasonable viscosity is needed for effective coating). Latexes can also be made self-thickening by the incorporation of carboxyl groups into the latex particles. A thickener can also be added to a latex composition to adjust the coating viscosity.

In addition, the surface tension of the latex would need to be controlled to give good wetting onto the glass fiber. Contact angle measurements on glass substrates can be used to determine the optimum wetting behavior before moving on to the glass fiber itself. The thickness of the polymer coating would also need to be varied to determine the necessary thickness needed to give a good, measurable response when exposed to solvent or water containing the heavy metal ions. If the coating is not thick enough, the response to the analyte may be too weak. If the coating is not uniform on the fiber, there would be unexposed regions of the fiber which would affect the detection limit and sensitivity. In addition, there needs to be good adhesion of the coating to the fiber, otherwise delamination could occur. Silane adhesion promoters can be explored to enhance adhesion of the polymer coating onto the glass fiber substrate. The drying temperature and drying conditions (e.g., time and temperature that the latex-coated fibers are dried in an oven to ensure good film integrity or the use of forced heated air flow over the fibers) are also critical coating variables to be investigated.

3.2.3. Kinetics

The kinetics of swelling of the polymer coatings when exposed to aqueous or organic media needs to be evaluated by monitoring the changes in the dimensions of the coating or the gravimetric uptake of the media by the polymer. The time-dependent changes can be analyzed to give an idea of the best polymer architecture to obtain an optimum sensor response when exposed to a given chemical. The time constant for the sensor response needs to be determined and correlated with the swelling kinetics of the polymer coating to achieve the best sensor performance.

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3.3. Development of a prototype ph sensor with reactive polymer coating

The development of an optical fiber pH sensor based on hetero-core fiber structure coated with an acrylic polymer doped with Prussian blue is discussed here. In this design, the pH changes of the surrounding medium affects the Prussian blue present in the layer and produce a change in the refractive index of the layer. The pH changes are then observed as an increment in the hetero-core transmission signal.

3.3.1. Building of hetero-core optical fibers with reactive layer

The hetero-core fibers were constructed using two different length and two different types of optical fiber. In this case two types of single-mode fibers (SMA and SMB) and two of multimode fibers (MMA and MMB) were used. First, two pieces of MM fiber, stripped of its coating polymer (3 cm section) were spliced to a stripped SM fiber on each side. The hetero-core fibers were treated with Prussian Blue 0.1 mM (PB), polyvinyl alcohol(PVOH) at 4 %,acrylic polymer emulsion (APE) at 50 % plus and their combinations, like PVOH + PB and APE + PB to develop a reactive coat over the stripped surfaces. A small U-shape container made of a glass capillary was fixed to a mechanical mount and was filled with the mixture of polymer support and Prussian blue sensitive material. Then the single-mode section of the hetero-core fiber was immersed for 5 minutes into the solution after which the fiber was removed and dried at room temperature. In this manner the sensitive material was adhered to the single-mode section of the hetero-core fiber.

One end of the hetero-core fiber was connected to a white light source Yokogawa AQ4305 and the other to the spectrum analyzer Ando AQ6315A (Figure 14A). The set-up was used to measure the transmission light during the modification process of the fiber and later to measure the response of the modified fiber to pH changes. In order to test the sensitivity of the device to changes in pH, a test was designed which consisted of immersing the optical fiber section modified with PVOH/PB or APE/PB in a Petri dish where the pH was varied by adding 0.1 M NaOH or 0.1 M HCl, recording each transmission spectrum changes in the wavelength range from 350 nm to 1700 nm (Figure 14B).

The transmission spectra of two hetero-core fibers with PVOH/A (5 mm and 10 mm sections) were measured in different pH solutions are shown in Figure 14A and 14B, respectively. As seen in figure 15 the device has good sensitivity (-1.5 dB and -2 dB approximately), however the signal is erratic and not repeatable for different pH changes. This was attributed to solubility of PVOH in acidic conditions, and checked visually and with the transmission spectrum analysis. A new polymer, acrylic polymers emulsion (APE) was selected to replace PVOH. This polymer has similar characteristics as PVOH. It is water soluble, inexpensive, and colorless when dried, and has been reported as a good support in manufacturing of modified electrodes for pH determination.

The transmission spectra of two hetero-core fibers with APE/A (5 mm and 10 mm sections) were measured in different pH solutions are shown in Figure 16A and 16B, respectively. As seen in Figure 16A, the device showed very obvious changes when subjected to acidic and basic conditions. The presence of three peaks in visible region, 400, 500 and 700 nm wave-

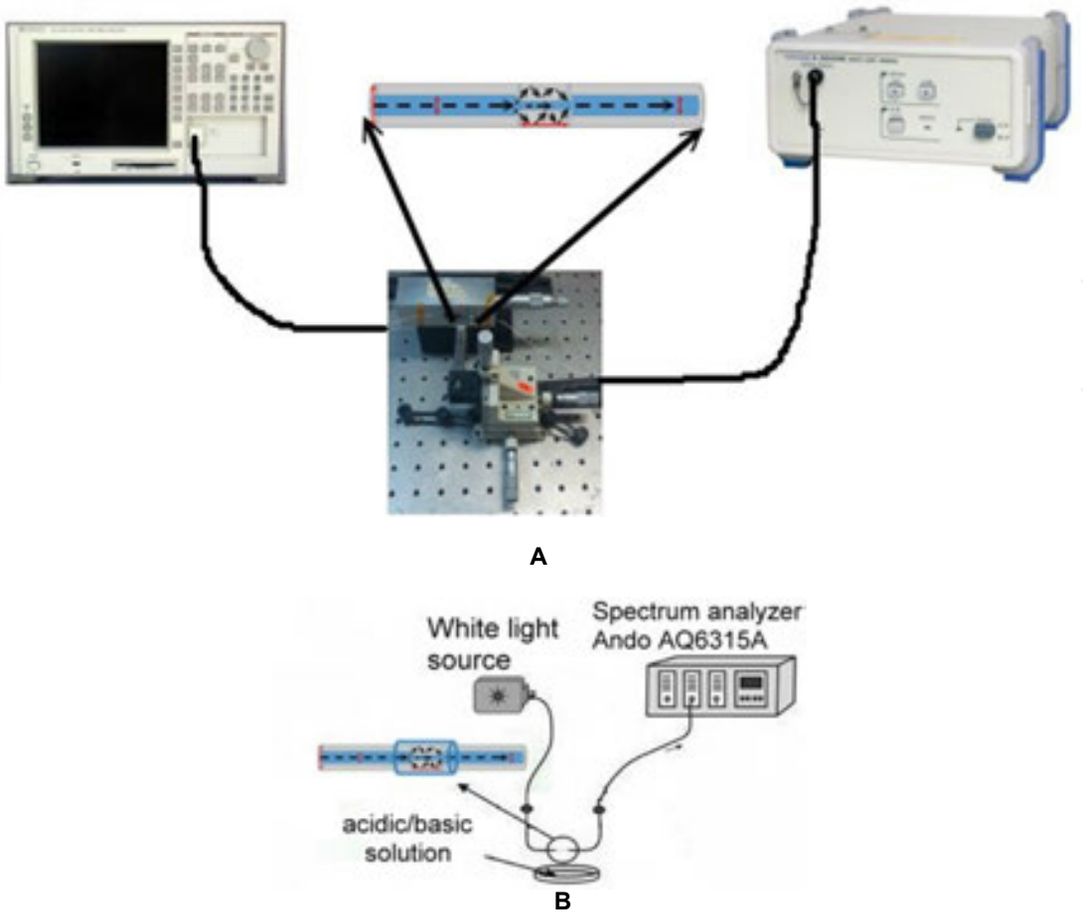


Figure 14. Set up to test prototype hetero-core fibers for chemical detection: (A) Diagram of the set-up to measure the transmission signal of the hetero-core fibers; (B) Diagram of the test system to determine the sensitivity of hetero-core fiber to pH changes.

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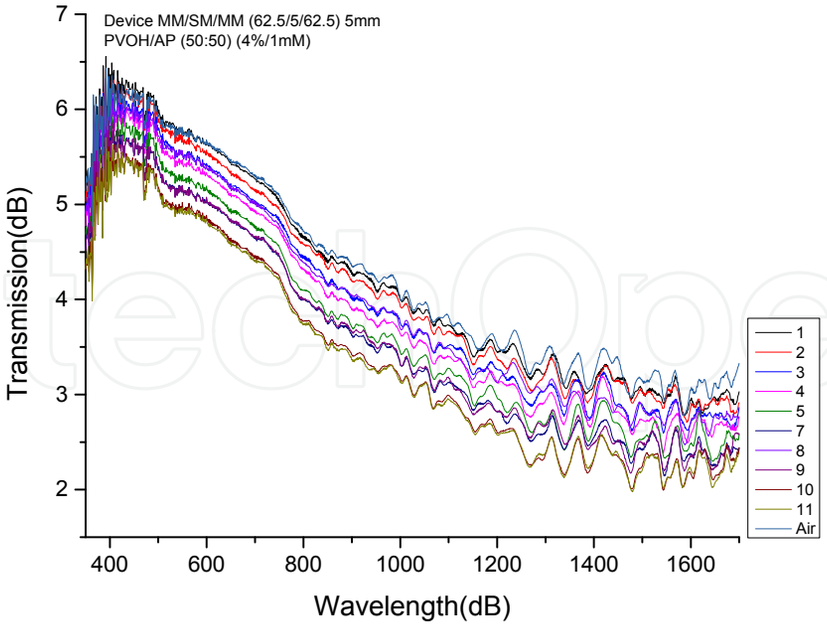
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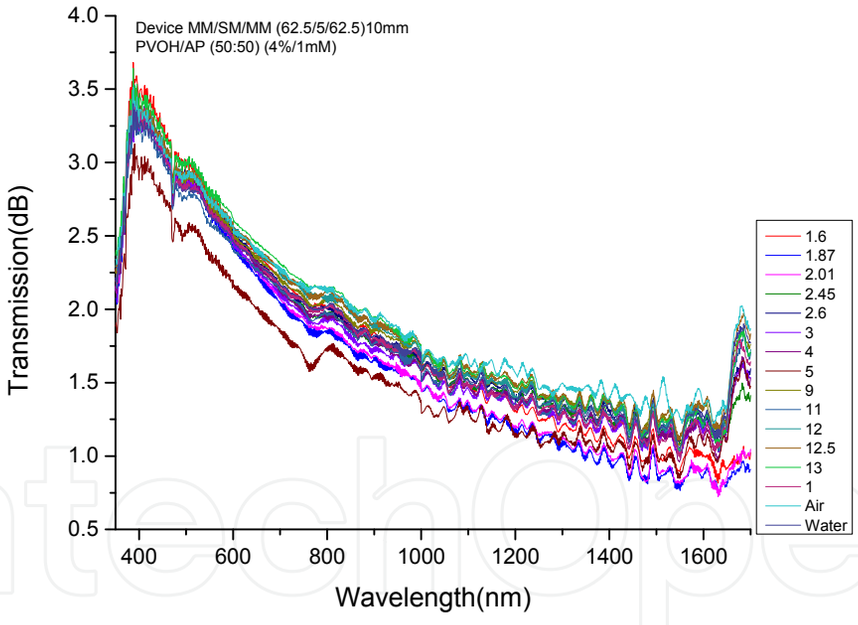
In order to identify the origin of signals found, the concentration of Prussian blue was increased to 2 mM. As we can see in Figure 16B, the intensity of transmission peaks at 400, 500 and 700 nm was increased, suggesting that they are due to increased concentration of PB in the composite. It also shows that the device sensitivity increased from 1.5 to 3 dB with 1mM concentration of PB until 4 to 6 dB with 2 mM concentration of PB for acidic pH solutions, but behaved same as previous in basic solutions. Finally there was a good return to initial conditions after each change of interface (Figure 17).

Subsequently we performed a sensitivity analysis for pH changes by taking the APE/PB modified fiber signal in air to use as a normalizing reference. As shown in Figure 18, there is good sensitivity to pH values lower than 7 with gains up to 6 dB at 400 nm (absorption or loss peak), whereas above pH 7 the peak is inverted, turning in a gains peak which may be due to

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A

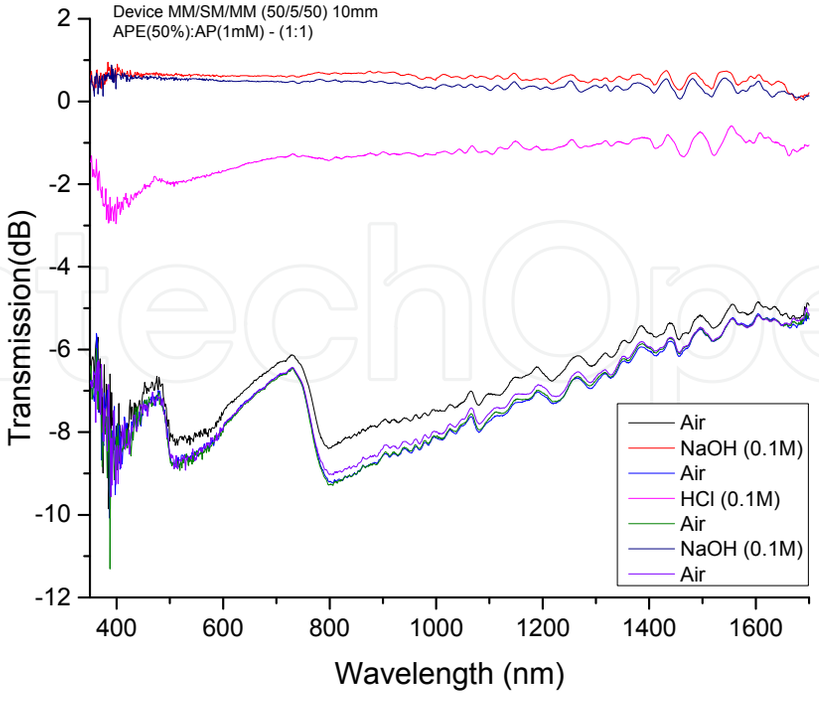


B

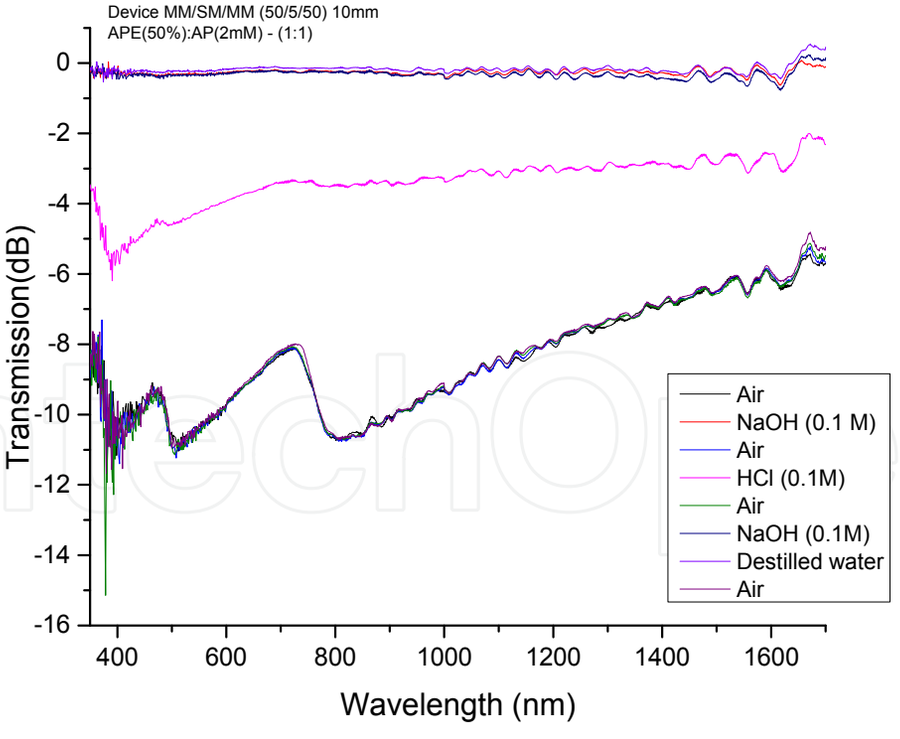
Figure 15. Transmission spectra of hetero-core fiber with PVOH/AP and its sensitivity to pH change with 5 mm (A) and 10 mm (B) length.

Figure 15. Transmission spectra of hetero-core fiber with PVOH/PB and its sensitivity to pH change with 5 mm (A) and 10 mm (B) length.

the hydration process of the polymer and breaking of complex of PB by hydration. To identify the changes in transmission spectrums, the most characteristic signals (400, 700 and 800 nm) and the response to 1500 nm (common wavelength in telecommunication systems) were plotted independently.



A



B

Figure 16. Transmission spectra of hetero-core fiber with APE/AP and its sensitivity to pH change with 1 mM (A) and 2 mM (B) AP.

Figure 16. Transmission spectra of hetero-core fiber with APE/PB and its sensitivity to pH change with 1 mM (A) and 2 mM (B) PB.

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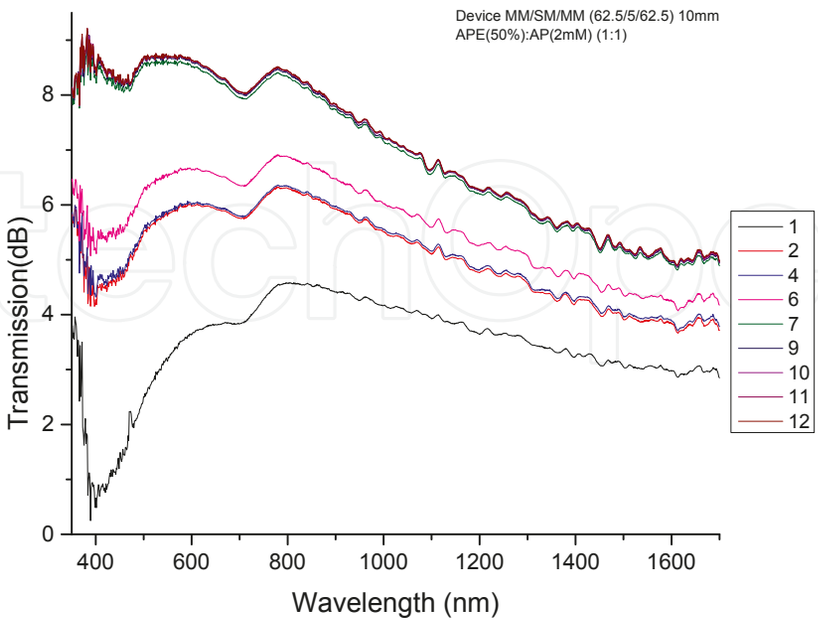


Figure 17. Transmission spectrum normalized to air of the modified hetero-core device with APE/PB (2 mM) and its sensibility to pH changes.

Analyzing the charts of Figure 18 shows that the transmission intervals are decreasing with increasing wavelength, which demonstrates good sensitivity of the device. As previously mentioned, the pH changes were more evident at pH values less than 7, due to that pH values higher than 7, it promotes the process of hydration of Prussian blue complex (Equation 4) and the signal grows weak on each pH change (García – Jareño et al, 1996).

$$Fe_4\left[Fe(CN)_6\right]_3 + 12OH^- \Leftrightarrow 4Fe(OH)_3 + 3\left[Fe(CN)_6\right]^{4-} \quad (4)$$

Based on the results obtained so far, the 10 mm rather than the 5 mm length hetero-core device is recommended since their sensitivity and the evanescent wave field is bigger than 5 mm length devices. Also the 10 mm length device provides a gain of about 2 dB at throughout the analysis spectrum.

Actually, all devices showed in this paper are preparing to their application in real scenarios, with the intention to quantify physicochemical properties directly to polluted soil without extraction from the field and pre-treatment of sample, which could reduce time and costs of analytical determination, increasing the sensibility, detection and quantification limits in comparison with spectroscopic and spectrometric techniques, to take the best professional decision to remediate in the better technical conditions the polluted soil.

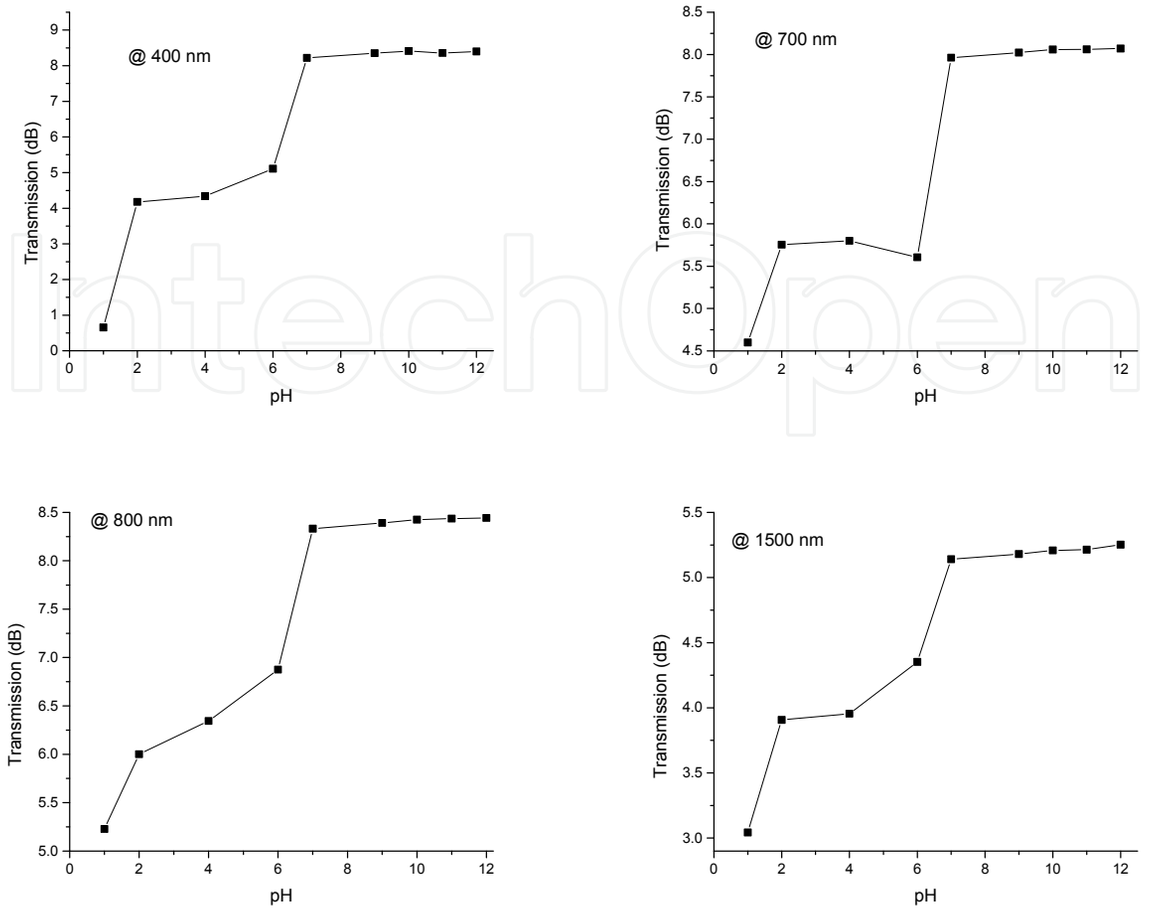


Figure 18. Transmission spectrum of hetero-core device modified with APE/PAH and its sensibility to pH changes at 400, 700, 800 and 1500 nm wavelength.

Analyzing the charts of Figure 18 shows that the transmission intervals are decreasing with increasing wavelength, which demonstrates good sensitivity of the device. As previously mentioned, the pH changes were more evident at pH values less than 7, due to that pH values higher than 7, it promotes the process of hydration of Prussian blue complex (Equation 4) and the signal grows weak on each pH change (García – Jareño et al, 1996).

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Based on the results obtained so far, the 10 mm rather than the 5mm length hetero-core device is recommended since their sensitivity and the evanescent wave field is bigger than 5 mm length devices. Also the 10 mm length device provides a gain of about 2 dB at throughout the analysis spectrum.

Actually, all devices showed in this paper are preparing to their application in real scenarios, with the intention to quantify physical and geo-environmental pollutants, for example, spatially resolved analysis of sample, which could reduce time and costs of analytical determination, increasing the sensibility, detection and quantification limits in comparison with spectroscopic and spectrometric techniques, to take the best professional decision to remediate the latter technical problem and the polluted soil source.

4. Conclusion

For pollution detection and soil remediation purposes it is essential to have relevant and reliable information on the soil structure, the hydrogeological circumstances and accumulation zones of the detected pollutants. Combined application of geological, hydrogeological and geophysical investigations prior the placement of the optical fiber in the field may increase the efficiency of the monitoring technique.

Spatially resolved mapping of chemical constituents is an important need in a variety of environmental and geo-environmental applications. For example, spatially resolved analysis of monitoring can simultaneously indicate and locate when an accepted level of exposure to toxic or explosive species has been reached, and the plume's

The capability of long-range distributed sensing is unique to optical – fiber technology. A distributed fiber optic sensor returns a value of a target measurement as a function of the linear position along the fiber length. The only contact between the point to be measured and the observation area is the optical fiber.

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