

Fibre Optic Humidity and pH Sensing for Healthcare and Sports Applications

by

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Abstract

The ultimate objective of this PhD thesis is the development and characterisation of optical fibre sensors for humidity and pH monitoring with the aim of exploring their applications in healthcare and sport. In particular, wound healing monitoring, foetal blood sampling and body sweat rate during exercise were explored. Sensors have been thoroughly characterised to establish key parameters such as sensitivity, response time, cross sensitivity to temperature, wearability and portability of the sensors.

The humidity sensor was fabricated by coating the central unclad section of a polymeric optical fibre with a hydrophilic film consisting of PAH/SiO₂ layers deposited by layer-by-layer method. The developed sensor achieved a sensitivity of -3.87×10^{-3} and -9.61×10^{-3} in transmittance percentage per relative humidity (RH) percentage for the range of $\sim 10\%$ to $\sim 75\%$ RH and 90% - 97% RH, respectively with a response time of 1.5s. Moreover, the implementation of this sensor within garments has been studied to monitor humidity on the human skin. The results suggested the feasibility of the optical fibre sensor to be embedded into garments, such as wound dressings in order to provide humidity measurements of the wound surface without removing the dressing and hence disturbing the wound healing process. In addition, the humidity sensor performance was also tested in the monitoring of the humidity expelled from the body while cycling producing promising results that can lead to the use of this sensor in sports clothing to evaluate in real-time the humidity of the body and hence personalise exercise routines and improve body performance.

Moreover, the optical fibre pH sensor was fabricated with a U-shape geometrical configuration. The sensitive region of the sensor was coated with a dye compound (TSPP) as a pH indicator using sol-gel technique. This sensor was based on the absorbance of light in two regions of the spectra (Soret and Q bands) over small pH variations providing a sensitive pH range of 6.7 - 8.1. The sensitivity obtained was 0.032 in absorbance units per pH unit and -0.054 in absorbance units per pH units for the Soret and Q band, respectively. The potential application for this

sensor is to equip clinicians with the tool that can help to take an early decision during foetal blood sampling technique since the sensor developed can provide in-situ pH measurements with a fast response (~ 40 s). In addition the optical fibre sensor for pH measurements can be useful to analyse the properties of the sweat or wound exudate in order to provide more information to improve nutrition and wound healing, respectively.

On the other hand, the instrumentation to monitor the response of both sensors was also investigated. The design of a low-cost portable electronic device consisting of small electro-optical components for the evaluation of the developed sensors is presented to replace the relatively bulky experimental set-up consisting of a CCD spectrometer and a broadband light source and provide a small electronic unit to monitor in real-time the sensors response.

In conclusion, the research presented in this PhD offers a novel alternative for the current techniques and devices implemented in healthcare and sports applications through the development of optical fibre sensors for humidity and pH measurements.

Author's research publications and conferences

Journal article

Gomez D., Morgan S.P., Hayes-Gill B.R., Goncalves R., Korposh S., "Polymeric optical fibre sensor coated by SiO₂ nanoparticles for humidity sensing in the skin microenvironment", *Sensors and Actuators B: Chemical*, Vol. 254, pp. 887 - 895, 2018.

Conferences

Gomez D., Morgan S.P., Hayes-Gill B.R., Goncalves R., Korposh S., "Polymeric optical fibre sensor coated by SiO₂ nanoparticles for humidity sensing in the skin microenvironment", *Proc. SPIE 9916*, Sixth European Workshop on Optical Fibre Sensors; 991623 (June 2016).

SET for Britain, British Parliament, London, UK, March 2016.

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"Mira que te mando que te esfuerces y seas valiente; no temas ni desmayes, porque Jehová tu Dios estará contigo en dondequiera que vayas." - Josue 1:9 -

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List of acronyms

ADC		Analog-to-digital converter
BCG		Bromocresol green
BCP		Bromocresol purple
BG		Brilliant green
BPB		Bromophenol blue
BPS		Bits per second
BTB		Bromothymol blue
BY		Brilliant yellow
CCD		Charge-coupled device
CM		Coumarin
CMOS		Complementary metal-oxide semiconductor
CPB		Chlorophenol blue
CPR		Chlorophenol red
CR		Cresol red
CTAB		Cetyltrimethylammonium bromide
CTG		Cardiotocography
DN		Digital number
DNA		Deoxyribonucleic acid
EAGLE		Easily applicable graphical layout

ECR		Eriochrome cyanine R
ESA		Electrostatic self-assembly
EtOH		Ethanol
EW		Evanescent wave
FBG		Fibre Bragg grating
FBS		Foetal scalp blood sampling
FHR		Foetal heart rate
GaAs		Gallium arsenide
GaAsP		Gallium arsenide phosphide
HEC		Hydroxyethylcellulose
HF		Hydrofluoric acid
IC		Integrated circuit
ISAM		Ionic self-assembly monolayer
LASER		Light amplification by stimulated emission of radiation
LbL		Layer-by-layer
LC		Lucent connector
LED		Light emitting diode
LiPo		Lithium ion polymer
LPF		Low-pass filter
LSB		Least significant bit
MRI		Magnetic resonance imaging
NA		Numerical aperture
Na⁺		Sodium
NEP		Noise equivalent power
NHS		National Health Service

NIR		Near-infrared
NR		Neutral red
OFHS		Optical fibre humidity sensor
OFS		Optical fibre sensor
PAA		Poly(acrylic acid)
PAH		Poly(allylamine hydrochloride)
PBS		Phosphate buffered saline
PCB		Printed circuit board
PCS		Plastic-clad silica
PDDA		Poly(diallyldimethyl ammonium chloride)
PDT		Photodynamic therapy
PMMA		Polymethylmethacrylate
POF		Plastic optical fibre
POFHS		Polymeric optical fibre humidity sensor
PSGS		Porous sol-gel silica
PSP		Phenol red
PSS		Poly(sodium 4-styrene-sulfonate) salt
PVA		Poly-vinyl alcohol
PVDF		Polyvinylidene fluoride
R6G		Rhodamine 6G
RB		Rhodamine B
RH		Relative humidity
RMS		Root mean square
SD		Secure digital
SMA		Sub-miniature version A

SMD	Surface mount device
SNARF-1C	Seminaphthorhodamine-1 carboxylate
SNR	Signal to noise ratio
SOIC	Small-outline integrated circuit
SPS	Samples per second
TB	Thymol blue
TECS	Technology enhanced clad silica
TEOS	Tetraethyl orthosilicate
TH	Through-hole
TIA	Transimpedance amplifier
TIR	Total internal reflection
TMOS	Tetramethyl orthosilicate
TQFP	Thin quad flat package
TSPP	Tetrakis(4-sulfophenyl)porphine
UV	Ultraviolet
VOC	Volatile organic compound

Chapter 1

Fibre Optic Technology in Body Monitoring: A New Approach

"Study without desire spoils the memory, and it retains nothing that it takes in."

- Leonardo da Vinci -

1.1 Introduction

In recent years fibre optic technology has made significant progress for sensing applications. Characteristics such as simplicity and low-cost, reliability of measurements and capability of overcoming hazardous environments with low maintenance have brought into consideration the use of optical fibre sensors (OFS) in a wide range of fields. These fields are for example the chemical industry (pharmaceutical production, food management, water treatment) [1], civil structures (bridges, buildings, train tracks, power plants) [2], oil and gas industry and the subject of this thesis namely healthcare (wound healing monitoring, respiratory monitoring, blood oxygenation). Furthermore, since the optical fibre is a dielectric device, it can be used in applications where the lack of electrical current is useful such as in-vivo applications in the human body or in explosive environments such as mining [3].

Moreover, the necessity to improve monitoring techniques for healthcare is without doubt of extreme societal benefit. Examples are: humidity and pH monitoring offering the potential to provide better prognosis in wound healing (i.e., the elderly and patients with chronic wounds requiring constant monitoring outside hospital) [4], during newborn delivery to prevent for instance, unnecessary interventions during labour; [5] and for sport performance to personalise exercise routines and improve body recovery [6].

Current techniques to monitor humidity such as the mechanical hygrometer or the wet and dry bulb psychrometer require special settings which are unsuitable for in-vivo applications. In addition, these techniques have a slow response time that is not convenient for applications where rapid humidity changes are required to be monitored [7]. In the case of the electronic devices, the most common mechanism found in the market is the capacitive-based humidity sensor. This type of humidity sensor is inexpensive and can cover a wide humidity range. However, since this is an electronic device, it can be affected by electromagnetic fields and tend to have short lifetime period since, in some cases, the battery is encapsulated, hence it is irreplaceable [8].

On the other hand, pH measurements are commonly obtained with pH electrodes and indicator strips. This technology can be useful for applications where the device size is not a concern (waste-water analysis) in the case of pH electrodes or a single-point pH measurement with low accuracy is required (chemicals pH monitoring) in the case of indicator strips [9]. However these methods are not compatible for some medical applications, for example during magnetic resonance imaging (MRI) or in-vivo applications due to the electromagnetic fields produced and the body response to the sensor materials [10]. This limitations have encouraged the development of optical fibre sensors for pH monitoring.

In this chapter, the motivation and aims for the development of fibre optic sensors for healthcare and sport applications are discussed with a review of the issues found in wound healing, newborn delivery and sport performance. Here, an explanation of the importance for monitoring parameters such as humidity and pH using fibre optics is discussed.

1.2 Wound care monitoring

The skin is the largest organ in the human body; its main function is to work as an anatomical barrier from external noxious agents due to its exposure to the environment [11]. Skin contains nerves that alert the response of the body when changes in temperature and pressure occur that can be harmful. Skin also has the capability to regulate our body temperature via perspiration and hence plays a vital role in the body's defences [12].

Skin is composed of two types of tissue: epidermis and dermis [11, 13]. The former is the upper-most layer of skin. It is 0.1 - 1.5mm thick and is made up of layers that contain cells that help to rebuild the surface of the skin. The dermis is the inner and thicker layer of the skin. It contains proteins such as collagen and elastin which give strength and flexibility to the skin, respectively [14, 15].

Since skin is an external organ, the risk of it being harmed is high due to several causes such as burns, surgical incision, accidental injuries or chemical damage.

In addition, the possibility of damage from external sources is increased in the presence of factors such as vascular diseases and following medical surgeries [16]. When this organ is disrupted, a wound appears and it is crucial that it can heal as soon as possible in order to restore skin structure and avoid infections [17].

Any stage of wound healing can be delayed due to either external or internal surrounding factors which require monitoring and controlling in order to ensure the correct wound healing sequence. These surrounding factors are levels of: oxygen, temperature, humidity and pH.

Oxygen is essential to prevent infection since cells such as neutrophils and macrophages, which form part of the bacterial defence, lose their capabilities during hypoxia [18]. In addition, oxygen is necessary for each stage of wound healing, especially for the proliferation, angiogenesis, epithelialization and collagen synthesis process [19]. Studies have established that oxygen levels in wound tissue for the different stages of wound healing should be in the range of 25mmHg - 100mmHg [20]. Oxygen has been demonstrated to function in an equivalent manner to an antibiotic for prevention of wound infections [13]. In summary, restriction in oxygen levels can severely impair the wound healing process.

Temperature is another external factor that needs to be monitored. The control of temperature is essential due to the cellular activity involved during the stages of wound healing, for example during the maturation phase lower temperatures can affect collagen alignment and stability to close the wound area [21]. Temperature changes in the wound area is a factor that can predict whether a wound is healing correctly or it is infected. When there is infection, temperature is increased and also colour can be changed in the wound area [22]. For that reason, it is important to detect any change in temperature in order to predict and combat possible infection [23].

Moreover, as 75% of the human body is composed of water then moisture can be detected in the epidermis [13]. Hence, when the epidermis is disrupted by a loss of moisture then delayed wound healing will occur due to the slower migration

of cells. Studies by George D. Winter [24, 25] have demonstrated the advantages of keeping a moist environment at the wound surface rather than allowing the wound to dry out. It has been shown that the healing rate is at least twice as fast when the wound is covered by a dressing that maintains hydration [26, 27, 28].

Moisture on wounds accelerates the epithelialization phase of wound healing by preventing scab formation over the wound bed. This increases migration of proliferative cells, such as fibroblast and endothelial cells that produces angiogenesis and promotes growth factors and keratinocytes, which results in faster dermal repair and reduced scarring of the wound [16, 29, 30]. In addition, it has been shown that moist wounds decrease bacterial infection by the formation of a hostile antibacterial environment [31]. Although there is a debate about the optimal level of humidity on the wound surface, it is undoubtedly the importance of maintaining a balance of the humidity in the wound surface in order to avoid skin breakdown and delayed healing [11, 32, 33].

Another controlling factor for wound healing is pH, which is related to the chemical reactions within the wound. Changes in pH will lead to infection and delay the wound healing phases [19]. The relation of pH with healthy skin has been studied and it has been demonstrated that the normal pH is in the range of 4 - 6. However, when the skin suffers an injury, there is a disruption in its biochemical processes and as a result there is increase in the pH to ~ 7.4 . The wound area becomes more alkaline by bacterial colonisation [34]. It has also been found that in chronic wounds the pH tends to oscillate between 7 and 8 [35]. Moreover, studies have observed that lowering the pH to the acidic region on the wound surface promotes oxygen release, angiogenesis and reduces bacterial infection [36]. For that reason, it is important to monitor pH in the wound area to restore the natural acidic environment and hence avoid infection [35].

Chronic wounds are a major global healthcare problem placing a considerable economic burden on the resources of healthcare providers. For example, in the UK alone, a recent analysis of the health economic burden of wounds highlighted that ~ 2.2 million wounds were managed by the publicly funded National Health

Service (NHS) in 2012/2013 requiring 18.6 million practice nurse, 10.9 million community nurse, 7.7 million GP and 3.4 million hospital outpatient visits. The annual NHS cost of managing these wounds is £4.5 - £5.1 billion ($\sim 4\%$ of the entire NHS budget) [37].

1.3 Foetal monitoring during labour

Foetal monitoring during labour is crucial to identify and prevent perinatal asphyxia and thus reduce risk of hypoxic ischaemic encephalopathy, cerebral palsy and death [38, 39]. Cardiotocography (CTG) is a commonly used technique to monitor foetal heart rate (FHR) to indicate possible intrapartum asphyxia [40]. However, evidence exists in the literature of its false positive and false negative nature and its inability to detect reliably intrapartum asphyxia [41, 42]. In most cases a second evaluation of the foetus such as foetal scalp blood sampling (FBS) for pH or lactate measurements provides more information to make a decision for delivery by caesarean section and prevent low Apgar scores [43, 44]. In the UK a standard interval of only 30min is allowed from taking of an FBS sample to the analysis and the subsequent decision of intervention (i.e., caesarian section) in labour [45, 46].

Studies have shown the relationship of blood pH to foetal asphyxia and immediate or long-term complications such as cerebral palsy. A pH of 7.35 is found as normal for the arterial of the foetus. However, during labour there is a reduction of pH to 7.15 in the umbilical artery blood, which does not represent a risk for the foetal health unless pH is further reduced ($\text{pH} < 7.1$) [47]. There are two type of acidosis: respiratory and metabolic. The former can be compensated after birth when the newborn releases the excess of CO_2 by breathing in the air with no neurological consequences. The latter may produce organ damage due to prolonged hypoxia which produces lactate and H^+ ions, leading to acidemia [48].

The invasive protocol followed for FBS, proposed by Bretscher and Sailing [49, 50] consists of a small incision on the foetal scalp to collect a sample of blood to measure its pH. A capillary tube is commonly used to collect a blood sample from

the scalp (35 - 60 μ L of blood are required per sample) to obtain a measure with a blood gas analyser (BGA) [51]. Nowadays, the use of pH test strips has been studied as another approach since less than 5 μ L of blood are required to obtain a measure [52]. The result assists clinicians in deciding whether a caesarean section is needed. Although a single sample result can be obtained within 15s, it would be extremely advantageous to implement real-time measurements since the pH can change continuously during labour and a single measurement is highly vulnerable to an incorrect decision on intervention [53].

Another parameter that can be extracted with FBS is lactate. Recent studies have shown that lactate measurements of FBS have a sampling failure of 1.2% - 1.7% compared to 11 - 20% for pH [54]. These sampling failures in FBS are: inhomogeneity of the sample; insufficient scalp incision; presence of air in the sample collected by capillary tubes; handling of the sample (from the sample extraction to its analysis); total time delay from the performance of FBS and interpretation of the result to the decision of making an intervention; and potential foetus infection [5].

1.4 Sweat monitoring in sports

Over the years, the importance to continuously monitoring body response during exercise using non-invasive sensors has increased in importance. For example, the use of wearable sensors is important for those people involved in sporting pursuits. Non-invasive measurable parameters such as heart rate, blood oxygenation and sweat rate have become of great importance for health monitoring and performance in sporting activities [6].

Sweat is a natural response for body thermo-regulation while exercising. It is a colourless and odourless fluid that contains ions such as sodium, potassium, calcium, magnesium, chloride and lactate [55]. These biomarkers can be evaluated to understand the physiological condition of the person undergoing exercise. A continuous monitoring of sweat can provide useful information about pathological disorders of the body, dehydration, loss of minerals and proteins [56]. The analysis of this information can yield during exercise to a fast and accurate response to

improve performance recovery and thus health. Several studies have been undertaken to analyse pH in sweat providing measures for example of sodium (Na^+) and chloride levels in sweat glands and its effect on the body response whilst under stress [57, 58, 59].

The human body has two types of sweat glands: eccrine and apocrine. The former, whose function is to regulate the body temperature by producing sweat, can be found in the entire body [60, 61]. The latter have a limited body cooling function and can be found in certain locations of the body namely: armpits; ear canal; breast; and some parts of the external genitalia [62]. Higher sweat rates can be found at the chest and upper back regions of the body. The average human sweat rate in these body regions are $1.21\text{mg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ and $0.95\text{mg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$, respectively [55, 63, 64].

Moreover, when the body is exposed to prolonged sport activities such as marathon competitions, the body's effort can provoke an excessive sweat loss that will lead to a reduction in body weight [65, 66]. It has been established that a decrease in body weight of $>2\%$ induced by exercise produces severe demands on the cardiovascular system and an extreme level of dehydration [67, 68, 69]. Electrochemical sensors are commonly used to monitor biological changes in sweat, however along with most sensors used to date, they are not ambulatory, i.e., samples need to be collected from the body to be analysed in either hospitals or laboratories [57].

Optical fibre sensing technology is a novel approach that can provide more information about the parameters described in this section to improve monitoring techniques in healthcare and sports applications. Furthermore, the implementation of optical fibre sensors represent an alternative to the current devices and techniques followed in these fields. In the next section, a brief description about optical fibre sensing technology is presented.

1.5 Fibre optic sensor

An optical fibre is a thin, cylindrical (diameter of the order of $100\mu\text{m}$ - $1000\mu\text{m}$) and transparent strand made of glass or plastic. It is commonly used in com-

munication systems due to its capability to transmit light signals with minimal losses and for long distances [70]. It can also be used in hazardous environments due to its exceptional flexibility, durability and immunity to electromagnetic field interferences [71].

The optical fibre operation principle in propagating light is based on the total internal reflection (TIR) supported by the fibre structure [72]. The difference in refractive index between two media results in bending of light rays at the interface of both materials according to the angle of incidence. This effect is known as refraction and it is explained using Snell's law (Equation 1.1) [73]:

$$n_1 \sin \theta_i = n_2 \sin \theta_r \quad (1.1)$$

Where n_1 , n_2 are the refractive indices of the first and second medium, respectively and θ_i , θ_r are the angle of incidence and the angle of refraction, respectively. Furthermore, as θ_i is increased, light will be refracted until eventually the light rays will be reflected back to the first medium, i.e., TIR occurs [71, 73, 74]. However, this effect takes place only when n_1 is higher than n_2 and θ_i is greater than the critical angle, θ_c , given by Equation 1.2:

$$\theta_c = \sin^{-1} \left(\frac{n_2}{n_1} \right) \quad (1.2)$$

If $\theta_i \leq \theta_c$, light will be refracted throughout the second medium, therefore it is not suitable for light propagation inside the first medium. However, when $\theta_i > \theta_c$, TIR is achieved. Optical fibre technology therefore takes advantage of this effect to propagate light inside the fibre.

An optical fibre is composed of a core surrounded by a cladding, both with different refractive index. The core refractive index, n_1 , is higher than the cladding refractive index, n_2 , (i.e. $n_1 > n_2$) to enable TIR, thus the optical fibre can act as a wave-guide when $\theta_i > \theta_c$, as illustrated in Figure 1.1.

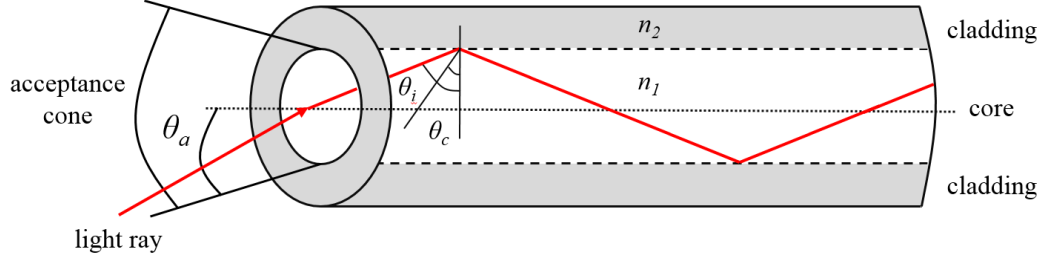


Figure 1.1: Optical fibre operation principle. Propagation of light is supported by TIR when $n_1 > n_2$ and $\theta_i > \theta_c$.

Although light can be transmitted within an exposed fibre core (i.e., one with no cladding) since it has a higher refractive index than air (air refractive index = 1.000293 at normal pressure and temperature), the unprotected core is susceptible to damage from the environment, such as scratches or dirt that will affect light transmission [73]. Therefore, a cladding with a lower refractive index than the core is added to enable light rays to be trapped within the core so as to be transmitted with minimal losses.

Moreover, since light rays enter into the fibre from an external medium (air in most of the cases), the angle of incidence at the core-cladding interface will depend on the angle at which the light rays were launched into the fibre core. Light rays need to hit the fibre core within this angle (known as the acceptance angle, θ_a) in order to be refracted inside the core and to hit the core-cladding interface at an angle of incidence higher than the critical angle, thus achieving TIR, as shown in Figure 1.1. Therefore, the optical fibre has an acceptance cone where light rays need to enter in order to be guided along the core.

Furthermore, the acceptance angle can be used to calculate the numerical aperture (NA) of the fibre, which is a dimensionless parameter given by Equation 1.3:

$$NA = \sqrt{n_1^2 - n_2^2} = n_0 \sin \theta_a \quad (1.3)$$

Where n_0 , n_1 , n_2 are the refractive index of the external medium, the fibre core and cladding, respectively, and θ_a is the acceptance angle. The NA defines the

ability of the fibre to collect light and it depends on the difference between the refractive index of the core and the cladding [73].

Light rays entering the fibre core within the acceptance cone can be guided at different angles of propagation, known as modes, with respect to the critical angle and the core diameter. These modes can be divided in high-order and low-order. The light rays propagated in high-order modes have an angle of incidence at the core-cladding surface close to the critical angle which produces loss of energy as the light rays are guided. In the case of low-order modes, the light rays are propagated at angles of incidence larger than the critical angle or parallel to the core axis (known as fundamental propagation mode), therefore loss of energy is reduced. The amount of modes classifies the optical fibre in two types namely: single-mode; and multi-mode [75].

Single-mode fibres are made of silica core with diameter around $10\mu\text{m}$ or lower. The cladding can be made of silica or plastic with diameter of $125\mu\text{m}$. Single-mode fibres are commonly used for communication systems since they can transmit optical signals for long distances (above 20km) with minimal losses due to the small difference in the core and cladding refractive indices that increases the critical angle, therefore only light rays travelling at large angle of incidence (low-order modes) can be internally reflected. If the core diameter is further reduced, most of the light rays will be scattered through the cladding. For that reason, the use of lasers is recommended to transmit light parallel to the core [74].

In the case of multi-mode optical fibres, the core and cladding can be made of silica or plastic. The main characteristic of multi-mode fibres is the large core diameter (from $50\mu\text{m}$ to 1mm) that enables light to enter at different angles, therefore travelling at high-order and low-order propagation modes. Furthermore, multi-mode fibres have higher NA that allows the use of LEDs as light source. However, this type of optical fibre is not suitable for long distance applications due to high transmission losses since a part of the light rays with angle of incidence lower than the critical angle are refracted through the cladding [71].

As explained above light propagation within an optical fibre is possible when TIR conditions are fulfilled. However, a small portion of light is not reflected back to the core, as shown in Figure 1.2, it propagates through the cladding. This phenomenon is known as an evanescent wave (EW) [76] and extends along the core-cladding surface and has an amplitude or penetration depth determined by Equation 1.4:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\cos^2 \theta_c - \cos^2 \theta_i}} \quad (1.4)$$

Where λ is the wavelength of light in vacuum launched into the optical fibre, n_1 is the fibre core refractive index, θ_c is the critical angle, which is expressed in Equation 1.2, and θ_i is the angle of incidence with respect to the core-cladding surface normal. The evanescent wave penetration depth, d_p , decreases exponentially from the core-cladding interface and is considered as the distance at which its magnitude decreases to its $1/e$ value, typically of the order of nanometres.

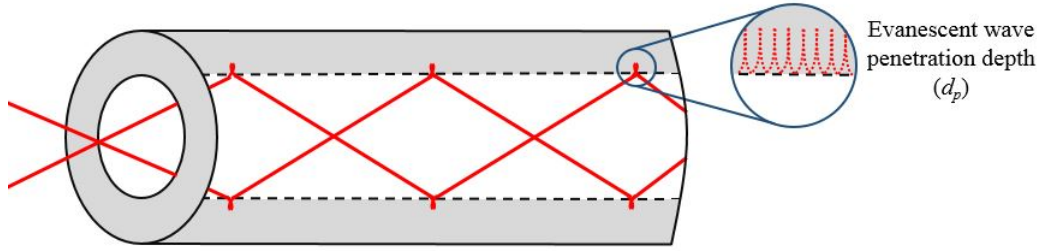


Figure 1.2: Evanescent wave penetration depth (d_p) in the optical fibre core-cladding surface.

The EW can be accessed by removing the cladding or tapering the fibre. This can be useful for sensing applications since light travelling within the unclad or tapered section of the fibre can interact with the environment and hence light attenuation can be monitored at the end of the fibre [77, 78]. Moreover, another factor that determines the EW penetration depth is the optical fibre geometrical configuration. In this work we focus on two configurations: straight and U-shape in order to develop a humidity and a pH optical fibre sensor, respectively.

The EW penetration depth of an optical fibre with straight geometrical configuration (Figure 1.3) can be calculated using Equation 1.4. In this case, the EW

penetration depth depends on the wavelength of the propagated light rays, the refractive index of the media surrounding the core at the unclad section of the fibre, which defines the critical angle in this region (Equation 1.2), and the angle of incidence, which is constant along the cladding-core surface [79].

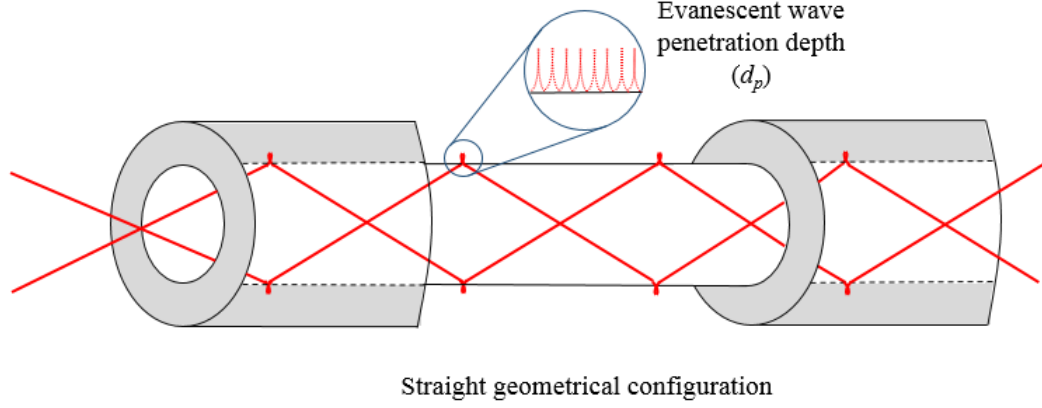


Figure 1.3: Evanescent wave penetration depth (d_p) at the unclad section of an optical fibre with straight geometrical configuration.

For example, let us consider a monochromatic LED launching light rays at 620nm wavelength into a multi-mode optical fibre with straight geometrical configuration (i.e., unclad central section of the total length of the fibre, Figure 1.3). The core and cladding refractive index are 1.49 and 1.4, respectively. In order to calculate the EW penetration depth at the unclad section of the fibre, the critical angle and the angle of incidence at this region need to be obtained.

In this case, the critical angle, θ_c at the unclad section of the fibre ($n_2 = 1.000293$ since the fibre core is exposed to air) calculated with Equation 1.2 is 42.17° . Moreover, as the angle of incidence approaches the critical angle, the EW penetration depth increases. However, since the EW penetration depth decays exponentially from the fibre structure, the $1/e$ value of the EW penetration depth in this example is $\sim 328\text{nm}$, as illustrated in Figure 1.4.

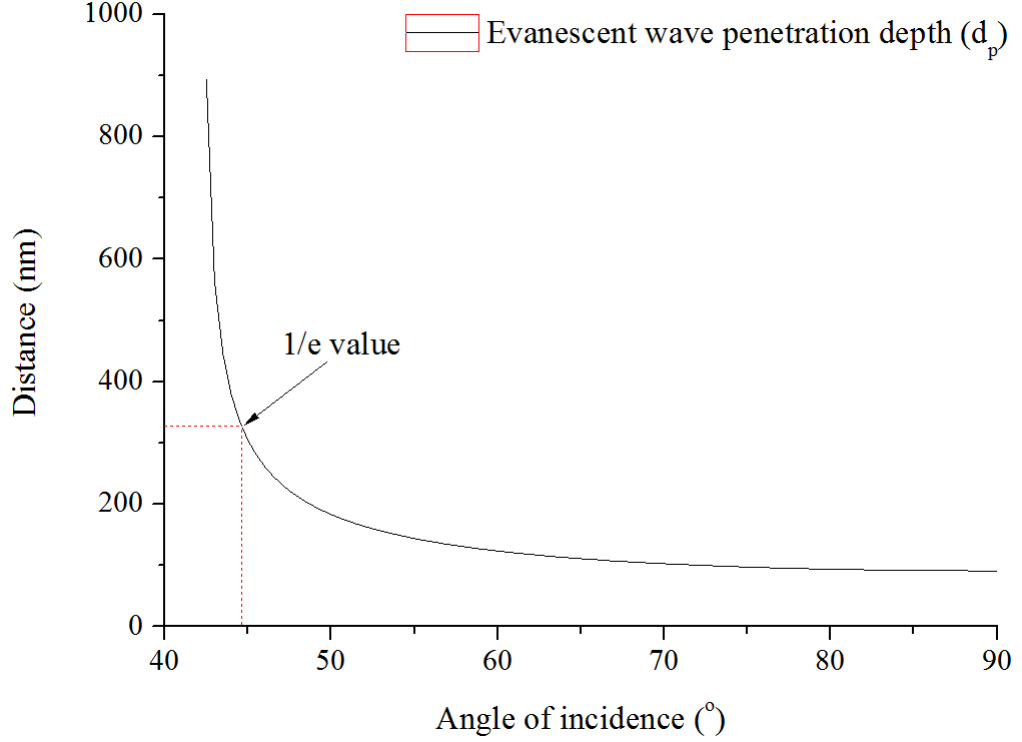


Figure 1.4: Example of evanescent wave penetration depth (d_p) at the unclad section of a multi-mode optical fibre with straight geometrical configuration. $\lambda = 620\text{nm}$, $n_1 = 1.49$, $n_2 = 1.000293$, $\theta_c = 42.17^\circ$ and $\theta_i \approx \theta_c$.

On the other hand, the U-shape geometrical configuration is formed by bending the unclad section of an optical fibre until a "U" is formed. In this case, light rays entering the bending region will hit the outer and inner surfaces of the U-shape at different angles with respect to the bending radius [80, 81, 82]. The angle of incidence (θ_i) in the U-shape region changes from ϕ_1 to ϕ_2 at the outer surface and from δ_1 to δ_2 at the inner surface with respect to the interface normal, as shown in Figure 1.5. The values of ϕ and δ are expressed in Equations 1.5, 1.6 and 1.7:

$$\phi_1 = \sin^{-1} \left[\left(\frac{R+h}{R+2\rho} \right) \frac{n_{cl}}{n_1} \right] \quad (1.5)$$

$$\phi_2 = \sin^{-1} \left[\frac{R+h}{R+2\rho} \right] \quad (1.6)$$

$$\delta_1 = \sin^{-1} \left[\left(\frac{R+h}{R} \right) \frac{n_{cl}}{n_1} \right] \quad (1.7)$$

and $\delta_2 = \pi/2$. Where n_1 and n_{cl} are the core and cladding refractive index, respectively, R is the bending radius, h is the height at the entrance of the bent region from the inner core-cladding surface, and ρ is the optical fibre core radius.

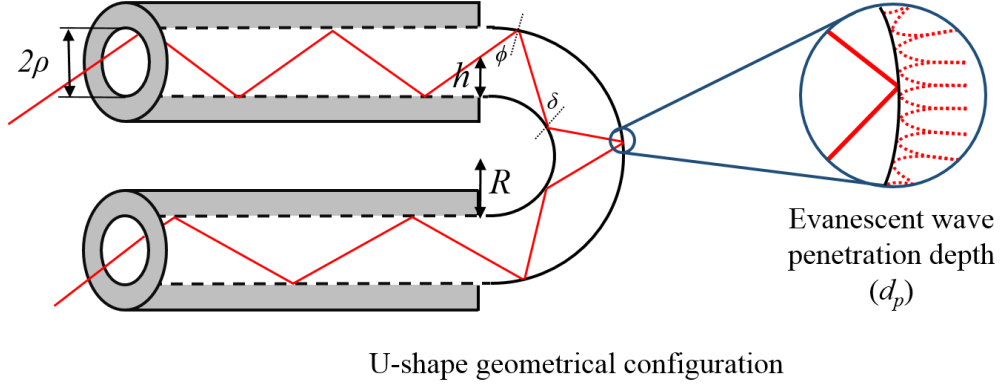


Figure 1.5: Evanescent wave penetration depth (d_p) at the bending region of an optical fibre with U-shape geometrical configuration.

In this case, the bending radius plays an important role for the EW penetration depth since the angle of incidence approaches the critical angle as the bending radius decreases, hence, increasing the EW penetration depth [83]. To further observe the effect of the EW penetration depth with respect to the bending radius, let us consider the previous example ($\lambda = 620\text{nm}$, 1.49 and 1.4 core and cladding refractive index, respectively) for a multi-mode optical fibre with $50\mu\text{m}$ core radius and different bending radius ($R = 10\text{mm}$, 1mm and 0.5mm). Table 1.1 shows the values of the EW penetration depth at the U-shape region with respect to the bending radius.

Table 1.1: EW penetration depth (d_p) at the bending region of an optical fibre with U-shape geometrical configuration for different bending radius ($\lambda = 620\text{nm}$, $\rho = 50\mu\text{m}$, $n_1 = 1.49$, $n_{cl} = 1.4$, $\theta_c(\text{U-shape}) = 42.17^\circ$).

R (mm)	h	ϕ_1	ϕ_2	δ_1	δ_2	EW penetration depth, d_p (nm)	
						outer surface	inner surface
10	0	68.48°	81.93°	69.98°	90°	102 - 91	100 - 89
	ρ	69.21°	84.29°	70.78°	90°	101 - 90	99 - 89
	2ρ	69.98°	90°	71.62°	90°	100 - 89	98 - 89
1	0	58.66°	65.38°	69.98°	90°	125 - 108	100 - 89
	ρ	63.75°	72.65°	80.60°	90°	111 - 97	91 - 89
	2ρ	69.98°	90°	unguided	90°	100 - 89	89
0.5	0	51.53°	56.44°	69.98°	90°	164 - 134	100 - 89
	ρ	59.46°	66.44°	unguided	90°	122 - 106	89
	2ρ	69.98°	90°	unguided	90°	100 - 89	89

It can be noticed that as the bending radius decreases, the EW penetration depth increases at the outer surface of the U-shape region. This can be useful to enhance the EW penetration depth, compared with the straight geometrical configuration. However, there exists a limit for the bending radius since the angle of incidence approximates the critical angle as the bending radius decreases.

Optical fibre sensing technology is based on the measurement of light transmittance, absorbance, reflectance or fluorescence in a medium or environment using optical fibres either to collect light from an analyte or to interact with the media. In addition to the optical fibre properties (small size, flexibility, low-cost, immunity to electromagnetic fields and resistance to hazardous environments), the OFS technology has demonstrated a reliable approach offering the ability to utilise sensitive coatings, conduct real-time measurements and perform chemical detection [84]. The study and fabrication of OFS technology has increased over the last few years due to the feasibility to attach sensitive films on the surface of the fibre [85].

This OFS technology can be classified as two types: extrinsic and intrinsic [86, 87, 88], as shown in Figure 1.6. An extrinsic OFS (Figures 1.6 (a) and

(b)) is used as a guide for incoming and outgoing light to and from the measurement point, i.e. light is provided to the sample through the optical fibre, then the resulting light interaction with the sample is collected by either the same fibre (reflectance measurements) or by another fibre to send it to an optical detector. The sensing area of this kind of sensor is either located at the end of the optical fibre or in-between a set of two fibres [76, 89].

On the other hand, in the intrinsic OFS type (Figures 1.6 (c) and (d)) light is modulated as it propagates along the fibre by interaction with the environment once the fibre has been treated with sensitive coatings (for example, evanescent wave absorption sensor) or the core structure has been modified (for example, Bragg gratings). In this case the sensing area is found within the optical fibre [90]. Furthermore, this type of sensor can be deployed to transmit and collect light at the same end of the fibre or at opposite ends of the fibre, i.e., reflection and transmission mode measurements, respectively.

The extrinsic and intrinsic OFSs can be subdivided according to the principle of operation [91, 92, 93] namely: intensity-based; wavelength-based; and phase-based. In the next section, these OFS categories are described providing examples and potential applications of each OFS category.

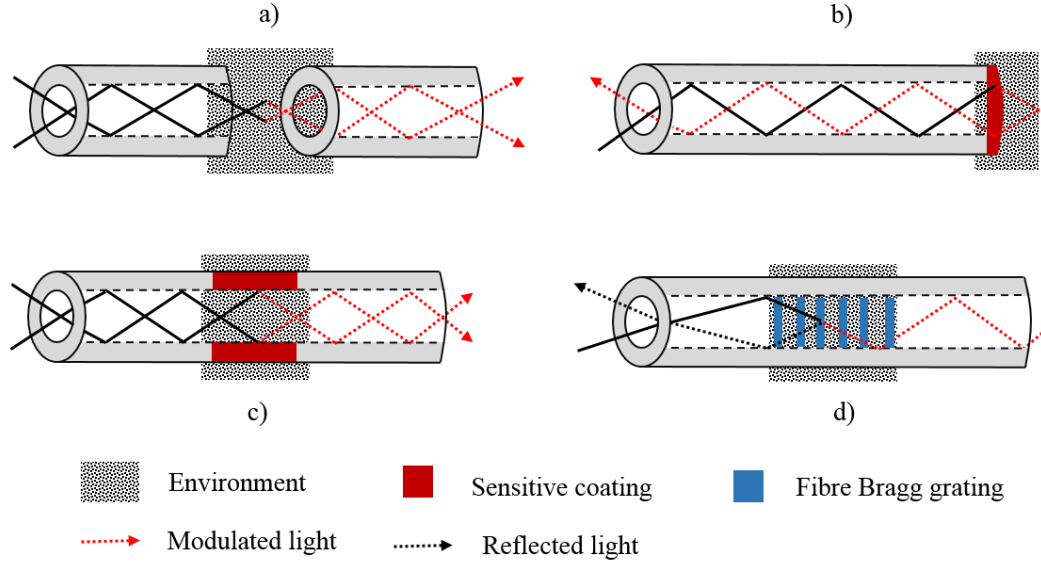


Figure 1.6: Extrinsic sensors: a) the fibre is used as a guide to provide light to the sample and collect the resulting absorption; b) the same fibre is used to transmit and receive light due to the modified tip. Intrinsic sensors: c) the cladding from a fibre section is replaced with a sensitive film which attenuates light within the core due to the interaction between EW and the environment; d) the fibre core is modified with Bragg gratings which are sensitive to environment parameters such as temperature or strain resulting in a wavelength shift.

1.5.1 Fibre optic sensing techniques

In the intensity-based OFS, the principle of operation relies on the monitoring of the attenuation of the transmitted or reflected light. The sensor can be built as extrinsic or intrinsic OFS. Examples of the intensity-based extrinsic OFS which can perform measurements with unmodified optical fibres are vibration or distance monitoring. In these sensors two bare fibres are held in close proximity to each other, as shown in Figure 1.6a. Light is launched into the first fibre and the attenuation of light with respect to the distance between both fibres is collected by the second fibre [94, 95].

On the other hand, the intrinsic intensity-based OFS can be created by bending the optical fibre. The fibre bending will produce attenuation of light due to the different angle of incidence of light within the fibre, as explained in Section 1.5 [96]. Therefore, the output light intensity of this OFS (also known as microbending OFS) is proportional to the bending of the fibre [97]. Another configuration

that can be used in the intensity-based sensing technique is the evanescent wave OFS. This configuration can be obtained by stretching the fibre (tapered fibre) [98], polishing the fibre (D-shape) [77] or exposing the fibre core [99]. The EW produced in the sensing region plays an important role since attenuation of light due to the interaction with the surrounding environment can be monitored. Moreover, the sensing region can be coated with sensitive materials for detection of analytes [79]. Applications of the intensity-based OFS under this configuration can be found in the development of sensors to measure pH, temperature, humidity, pressure or gas analysis [100, 101, 102].

The wavelength-modulated sensing technique is based on the detection of the wavelength shift of the transmitted or reflected light by a measurand of interest. The most common example of the wavelength-modulated OFS is the fibre Bragg grating sensor (FBG) [103]. This sensor is fabricated by periodic modulations of the refractive index of the core by either physical deformation or intense ultra-violet (UV) light radiation [104, 105]. The period of grating in the FBG sensor is in the range of $0.1\mu\text{m} - 2\mu\text{m}$. According to the period of the grating and the effective refractive index of the fibre core, a specific wavelength of light will be reflected (also known as the Bragg wavelength), while the rest of the wavelengths are transmitted [106]. Perturbations of the grating (for example, by temperature or strain) produces a shift in the Bragg wavelength that can be monitored. The main applications of this sensor are in structural health monitoring [107, 108, 109].

In the phase-modulated sensing technique, also known as interferometric method, the principle of operation is based on the measurement of the phase shift of the light propagated through the fibre [110, 111]. The optical fibre is connected to an optical coupler that splits the light path into two arms [112]. Typically, one of the arms is protected from the environment whereas the other arm is exposed to interact with the media to compare phase changes [113]. Examples of this kind of sensor are the Fabry-Perot [114], Sagnac [115], Mach-Zehnder [116] and the Michelson [117] interferometers. Applications of this type of sensing technique can be found in the development of hydrophones and gyroscopes [118, 119].

Figure 1.7 depicts a tree diagram of the OFS classification with respect to the principle of operation mentioned above. The sensing techniques highlighted (green color) are the techniques used in this PhD project for the development of OFSs for humidity and pH measurements (Chapter 3 and 4, respectively) for healthcare and sports applications. Moreover, as explained above, the evanescent wave OFS can be coated with sensitive films to detect specific analytes. In the next section, a description of the coating techniques used in this project is provided.

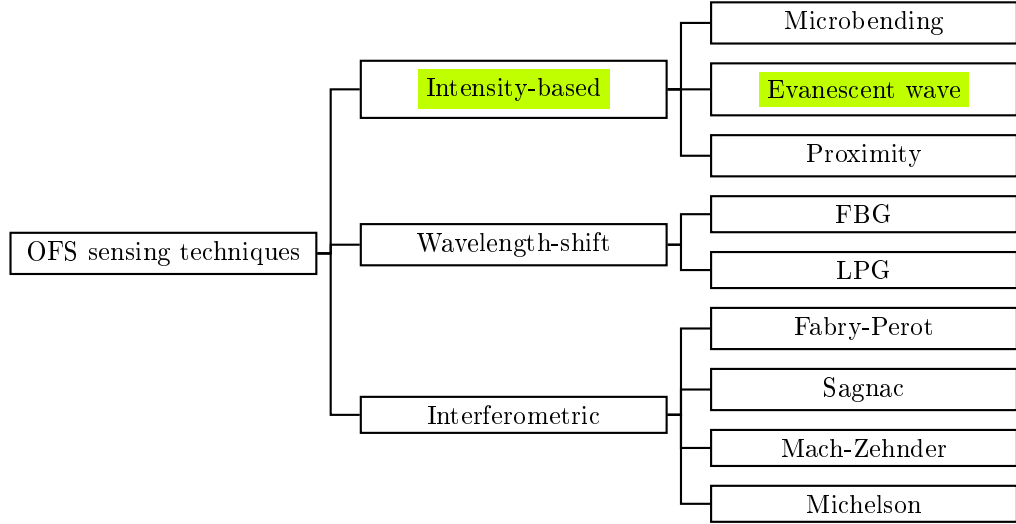


Figure 1.7: Optical fibre sensor (OFS) classification by sensing techniques. The sensing technique studied in this project is the intensity-based evanescent wave OFS (highlighted in green color).

1.5.2 Sensitive film coating techniques

The deposition of sensitive films onto the optical fibre can be useful for detection of analytes due to the interaction with the evanescent wave and the environment. The attenuation of light produced by the variations on the environment can be monitored and analysed.

In order to deposit a film onto the surface of the fibre, the core needs to be exposed (with few exceptions such as the microbending OFS presented in [120]) to allow the EW to interact with the sensitive film with respect to the surrounding environment (Section 1.5.1). Two well-known coating techniques are described: Layer-by-layer and sol-gel since these approaches produce a robust and reliable film.

Layer-by-layer

The layer-by-layer (LbL) coating technique, also known as electrostatic self-assembly (ESA), is based on the alternate deposition of oppositely charged molecules to obtain thin films in the range of nanometres with a strong bonding [121]. LbL deposition has proven its feasibility for coating optical fibres with a strong attachment of the thin film [122, 123].

The LbL procedure relies on the preparation of a substrate with a negative charge which will be alternately immersed into polyanion and polycation solutions in order to build a multilayer coating by electrostatic attraction [124], as shown in Figure 1.8. In order to create a sensitive film, it is possible to use a charged indicator solution as the outer layer. Increase in detection sensitivity can be obtained by increasing the number of layers until an optimum number of layers is reached [125].

There exists a relationship between the optimum number of layers, i.e. the film thickness and the EW penetration depth. The film thickness needs to be lower or equal to the EW penetration depth in order to obtain a higher interaction with the EW and the environment [78]. The optimum number of layers will be defined by the properties of the film such as the single layer thickness and the effective refractive index of the media surrounding the fibre core, which will define the critical angle at the sensitive region of the fibre and hence the EW penetration depth, as explained in Section 1.5.

One of the advantages of this coating technique is the ability to create a film with a well-organized structure and thus a controlled thickness [123]. The combination of organic and inorganic materials can yield sensitive films for detection of specific analytes [126]. Although the LbL deposited film has a strong bonding with the substrate, there are some factors that can destroy the ionic bonds of the film, for example if the substrate is immersed in a solution with high pH or high ionic strength [127].

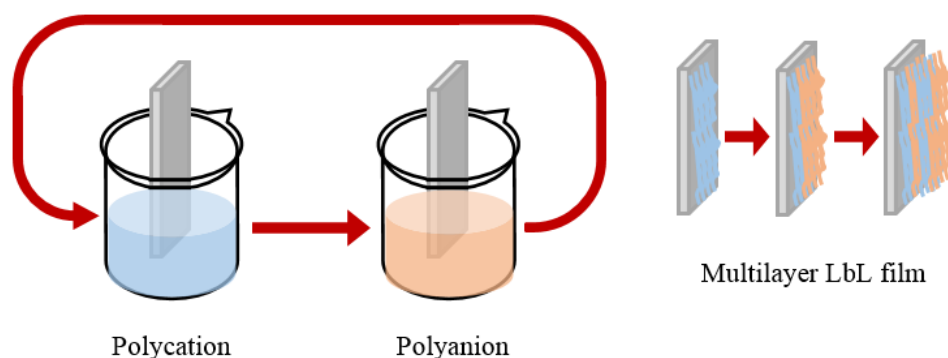


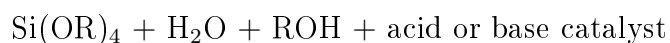
Figure 1.8: Layer-by-layer method for film coating onto a substrate.

Sol - gel

The sol-gel coating technique, also known as solution-gelation, has been widely used for the fabrication of biosensors [128]. Sol-gel is a method that creates a porous matrix at room temperature, hence it can encapsulate transducers or sensitive elements such as organic compounds which can be affected at either high or low temperatures [129, 130]. In addition, silica surfaces has been proven as an outstanding platform for this coating technique and many studies have therefore been made to observe the reliability of the sol-gel porous matrix on optical fibres [131, 132, 133].

The sol-gel fabrication method (depicted in Figure 1.9) is based on the hydrolysis of metal alkoxides within an alcoholic solution leading to condensation reaction of the metal alkoxides to form oxides [134, 135]. As a result, a homogeneous matrix with pore size of <50nm is obtained [136]. This matrix is very attractive for immobilization of indicators on surfaces such as optical fibres for pH measurements due to the low leaching rate of the indicator [131].

In order to prepare the matrix, a precursor solution is prepared. This solution consists of the following chemical structure:



Where R is an alkyl group. Sol-gel preparation requires a sequence of reactions.

First, an alkoxide is used as a precursor. Tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS) are alkoxides commonly used [137]. Then, the precursor is mixed with water and a co-solvent such as ethanol or methanol to form a homogeneous sol [128]. An acid or a base catalyst can be added to the solution to accelerate hydrolysis and polycondensation. The reaction will increase the viscosity of the solution and an interconnection in the structure will produce a porous gel [138].

The resultant sol-gel can be deposited on the fibre surface by spin-coating, dip-coating, spray-coating or electro deposition to obtain a thin sensitive film with thickness below $1\mu\text{m}$. The sensitive elements encapsulated with the sol-gel technique can be used for example for pH measurements, gas or chemical detection and many other applications [139].

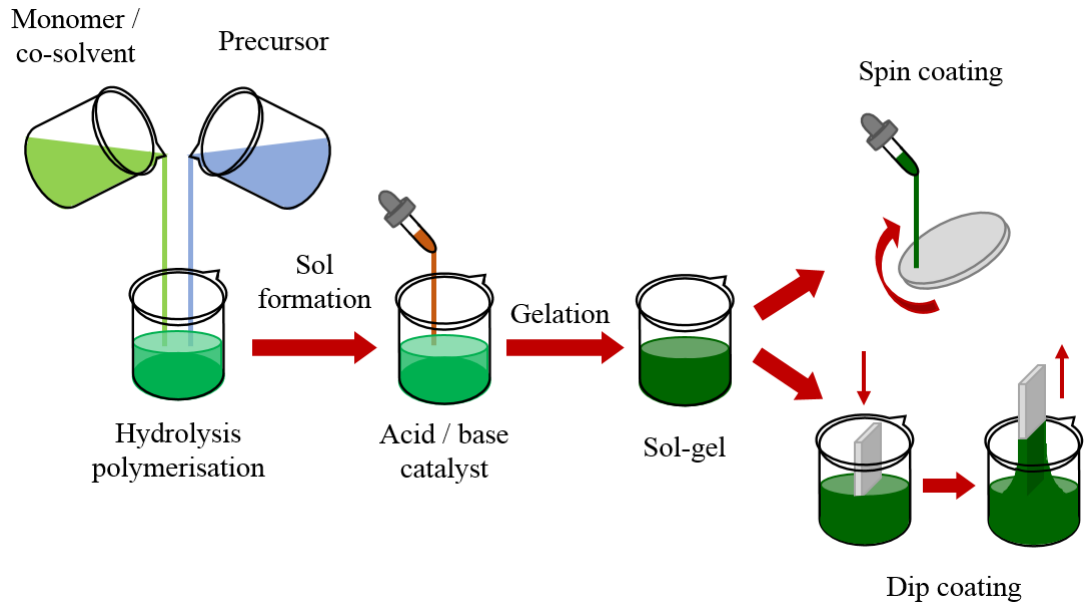


Figure 1.9: Sol-gel fabrication method and film coating alternatives.

1.6 Fibre optic system

Once the OFS is modified to make it specific to a desired measurand by the means described in Section 1.5.2, an opto-electronic evaluation system is required to obtain measurements of the environment through the sensing technique selected such as the examples in Section 1.5.1. Such an evaluation system normally con-

tains three components namely: light source; optical fibre sensor; and detector.

The first part of a fibre optic system is the light source which converts an electrical signal to an optionally modulated optical signal and launches it to the optical fibre. The light source can have a wide or narrow range of wavelengths depending on its composition. There are two common types of light source: light emitting diode (LED) and light amplification by stimulated emission of radiation (LASER).

In general, LEDs are cheaper and smaller in size than lasers. An LED emits light in a wide area, therefore it is necessary to use an external structure, such as the use of lenses, to couple light into the optical fibre. An LED requires between 20mA to 100mA (and 1.2V to 1.8V) to emit light. The power output is relatively small, it can be as low as microwatts or as high as few milliwatts ($\sim 3\text{mW}$). In addition, light is emitted at different wavelengths according to its composition. For example, an LED made of gallium arsenide (GaAs) will produce light at 930nm wavelength whilst one formed with gallium arsenide phosphide (GaAsP) will emit light at 660nm wavelength. They can be found in different packages, such as through-hole (TH) and surface mount device (SMD).

On the other hand, a laser requires a current from typically 30mA - 250mA and a forward voltage of 1.2V - 2V to operate. The resulting output power is from 1mW to 100mW. Contrary to LEDs, lasers emit coherent light and in a narrower wavelength ($< 10\text{nm}$). However, laser usage can be hazardous to the eyes due to its brightness, therefore safety procedures need to be applied whilst using them. In addition, a laser set-up is more complex since a laser requires more detailed external circuitry, i.e. a driver for example, to control the current supplied and temperature of the device.

Light coupling from the light source to the fibre relies on the following: emission angle in which light is spread; the light radiation area of the source; the alignment with the optical fibre; and the fibre characteristics such as its numerical aperture and core diameter. Figure 1.10 shows the importance of coupling the

light rays into the acceptance cone (for example, by using a laser or a collimator lens) to maximize the amount of light rays propagated within the optical fibre.

Moreover, the EW penetration depth will be affected by the selection of the light source and the coupling of light into the optical fibre. As observed in Equation 1.4, the angle of incidence is crucial to define the value of the EW penetration depth. The use of a laser or an LED as light source will establish the range of angle of incidence within the fibre. If a laser is used as the light source, the light rays will be propagated in low-order modes, which will decrease the EW penetration depth. In the case of an LED, light rays are propagated in low-order and high-order modes, therefore, the wider range of angle of incidence will increase the EW penetration depth.

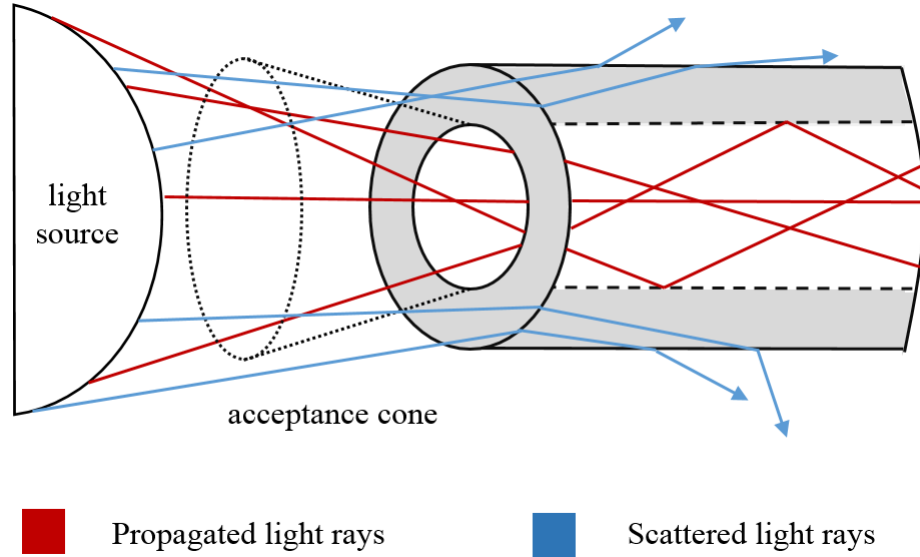


Figure 1.10: Light source and optical fibre. Light rays emitted within the fibre optic acceptance cone are transmitted.

Moreover, the light source can be modulated in two different ways: direct or external modulation. The former is related to the power supplied to the light source, i.e., by switching the light source on and off or even simply increasing or decreasing the light level in a controlled manner. An external modulation refers to an external device that changes the light beam at a desired frequency e.g. a mechanical rotating shutter.

In order to interconnect the optical fibre within the system, an optical connector is required. This provides an optical and mechanical link with the incoming light source and also the resulting optical detector at each end of the optical fibre. The same link can also be used to join two fibres together. The main properties of optical connectors are: ability to align the fibre core with optical devices; mechanical protection against bending; preservation from environmental disturbances such as moisture, dirt or vibrations.

The following element in the evaluation system is the optical detector. Its purpose is to receive an optical signal (in this case via the fibre output) and transform it into an electrical signal to be processed by an electronic circuit. Optimal characteristics of optical detectors are high sensitivity (A/W) at the operating wavelength, low noise and fast response. Although there are many optical detectors, in fibre optic systems, the photo-diode and the spectrometer (Figure 1.12) are the most commonly used for low-cost applications and high resolution measurements, respectively. In this work the description of both detectors will be presented since the spectrometer was used for laboratory tests in Chapter 3 and 4 and the photo-diode for dedicated practical applications in Chapter 5.

Photo-diode

In the case of the photo-diode, the key operational characteristics are the sensitivity, speed and noise performance. The sensitivity, also known as responsivity, is the relationship between the output current (Amperes) to the input power (Watts) expressed in Amperes per Watt (A/W) and can be calculated using Equation 1.8:

$$R = \frac{I}{\phi} \quad (1.8)$$

Where I is the photo-detector output current and ϕ is the optical power input on the photo-diode. Furthermore, the wavelength range over which the photo-diode responds to light depends on its material composition, for example a photo-diode made of silicon will react between approximately the wavelengths of 400nm - 1100nm. Alternatively, one composed of GaAs will detect wavelengths between

400nm - 900nm.

It is important to note that even when the photo-diode has no incident light, a small current (known as the dark current) is present at the output. This dark current is thermally produced and it should not be ignored in low light level and low signal conditions.

Furthermore, the photo-diode speed is considered as the time required to convert the incident light into an electrical signal. The response speed presents itself as rise and fall time of the signal. Rise time is typically calculated as the time the output signal goes from 10% to 90% of the final value in response to a sudden input change. Similarly the fall time is the time the output recovers from 90% to 10% of the peak value after the input is instantaneously removed.

The photo-diode can be used in two configurations namely: photo-voltaic; and photo-conductive. In the photo-voltaic mode, also known as unbiased or short circuit mode, the generated photo-current is divided by the internal shunt resistance and the external load resistance, producing a voltage that will forward bias the photo-diode. This mode is commonly used for applications where small light changes need to be monitored, hence dark current in this configuration is important and should be low in order to avoid masking the desired signal.

On the other hand, in the photo-conductive mode, the photo-diode is reverse biased. This increases the response speed but also increases the dark current, therefore the photo-conductive mode is recommended for applications where noise is not a concern and the required response time from the photo-diode is in the order of nano-seconds.

Moreover, the photo-diode has two noise sources that must be taken into consideration for its practical application namely: shot noise (i_{sh}); and Johnson noise (i_{th}). The former is related to the fluctuation in the dark current. Its magnitude can be expressed in Equation 1.9:

$$i_{sh(rms)} = \sqrt{2qi_dB} \quad (1.9)$$

Where q is the electron charge ($1.6 \times 10^{-19} \text{C}$), i_d is the dark current and B is the measurement bandwidth in Hertz.

The latter is related to the thermal generation of carriers, hence this noise source is also known as the thermal noise. It can be calculated following Equation 1.10:

$$i_{th(rms)} = \sqrt{\frac{4k_BTB}{R_{sh}}} \quad (1.10)$$

Where k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{J.K}^{-1}$), T is the temperature in Kelvin, B is the measured bandwidth (Hz) and R_{sh} is the photo-diode shunt resistance.

Given the previous calculations for the shot and thermal noise sources, the total noise current (i_{tot}) produced in the photo-diode is expressed by Equation 1.11:

$$i_{tot(rms)} = \sqrt{i_{sh(rms)}^2 + i_{th(rms)}^2} \quad (1.11)$$

The photo-diode total noise and its responsivity can be used to calculate the minimum optical power that can be detected by the photo-diode, i.e., the noise equivalent power (NEP), which is the optical power (of a given wavelength) required to produce a photo-current equal to the photo-diode root mean square (rms) noise. The NEP can be determined by Equation 1.12:

$$NEP(\lambda) = \frac{i_{tot(rms)}}{R(\lambda)} \quad (1.12)$$

In order to operate the photo-diode in either configuration, a current-to-voltage circuit is commonly used. An operational amplifier (op-amp) used in the transimpedance arrangement is a useful tool to convert the photo-current into voltage. Figure 1.11 (left) shows the transimpedance amplifier (TIA) circuit. The output voltage can be calculated using Ohm's law since the photo-current will flow through the feedback resistor, as shown in Equation 1.13:

$$V_{out} = I_{pd} \cdot R_f \quad (1.13)$$

Where I_{pd} is the photo-current and R_f is the feedback resistance. However, the TIA has also several noise sources that have to be considered namely:

1. The shot noise from the DC photo-current.
2. The thermal noise of the resistive component.
3. The op-amp voltage noise and current noise.
4. The overall 1/f (or flicker) noise of the arrangement - sometimes included in the op-amp voltage and current noise.

The first two are called white noise sources and here the noise spectral density is constant over the whole bandwidth of interest. The last two have both a 1/f and white noise source component. Figure 1.11 (right) shows the TIA equivalent noise circuit.

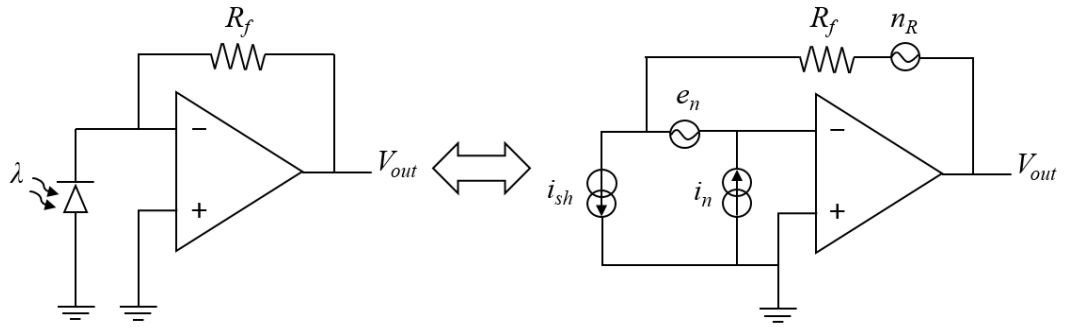


Figure 1.11: Transimpedance amplifier circuit (left) and equivalent noise circuit (right).

The optical shot noise can be calculated following Equation 1.14

$$i_{sh(rms)} = \sqrt{2qi_{DC}B} \quad (1.14)$$

Where q is the electron charge (1.6×10^{-19} C), i_{DC} is the DC photo-current and B

is the bandwidth (Hz). Since the shot noise flows through the feedback resistor, the voltage shot noise at the op-amp output can be obtaining by Equation 1.15:

$$V_{sh(rms)} = i_{sh(rms)} \cdot R_f \quad (1.15)$$

Where $i_{sh(rms)}$ is the current shot noise and R_f is the feedback resistance. Additional noise is produced by the feedback resistor, i.e., thermal noise which can be estimated with Equation 1.16:

$$V_{th}R_{f(rms)} = \sqrt{4k_B T R_f B} \quad (1.16)$$

Where k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J.K}^{-1}$), T is the temperature in Kelvin, R_f is the feedback resistance and B is the measured bandwidth in Hertz.

The op-amp voltage noise (e_n) and the op-amp current noise (i_n) can be found in the op-amp specification sheet provided by the manufacturer. The current noise flows through the feedback resistor, therefore, its output noise voltage (V_n) can be obtained by Equation 1.17:

$$V_{n(rms)} = i_n \cdot R_f \quad (1.17)$$

Therefore, the noise sources can be added to obtain the total output voltage noise as shown in Equation 1.18:

$$V_{nT(rms)} = \sqrt{V_{sh(rms)}^2 + V_{th}R_{f(rms)}^2 + e_{n(rms)}^2 + V_{n(rms)}^2} \quad (1.18)$$

CCD

Another type of detector is the charge-coupled device (CCD) which is sometimes found as a component in spectrometers. A spectrometer is an electronic device used to observe the spectrum of the incident light with high resolution and speed. In the spectrometer light passing through an entrance slit strikes a collimating mirror and is reflected towards a diffraction grating which splits the incident photons into its corresponding wavelengths. The resulting spectrum is sent to a

pixelated CCD and the value of light striking each pixel is passed under a software control to a computer.

Contrary to a photo-diode, high quality spectrometers are high-cost instruments which are not suitable for hazardous environments due to the fragility of its components such as the presence of a diffraction grating and a CCD which require precise alignment.

The spectrometer detector consists on a CCD array which is an integrated circuit (IC) that contains an array of capacitors that store charge according to the incident light. The accumulated charge is read at a time interval known as integration time. The longer the integration time, the higher amount of photons are collected until saturation of the CCD is reached. The gathered charge is transferred to a register within the IC in order to be arranged according to the measured wavelength.

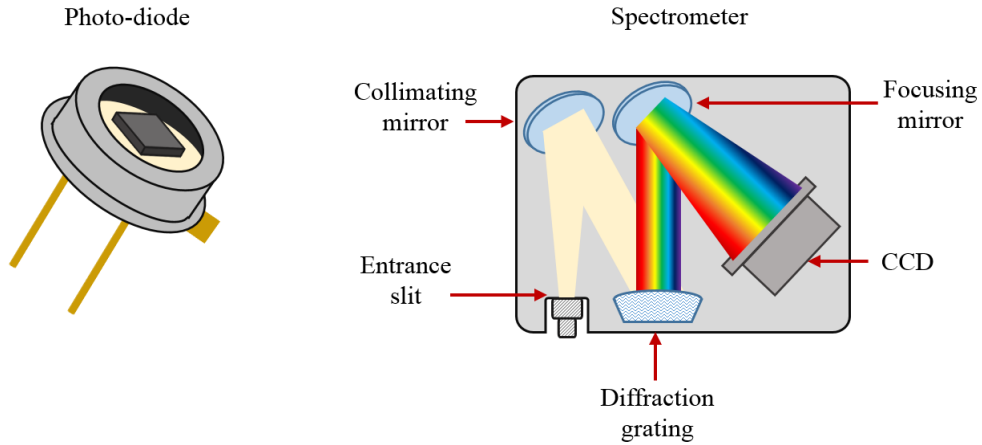


Figure 1.12: Optical detector. Example of a photo-diode (left) and a spectrometer (right) for the optical detector in the fibre optic evaluation system.

1.7 Aims and objectives

Over the years, there has been a large increase in the development of new devices to monitor the body using non-invasive sensors [106]. This provides many opportunities for better diagnosis to improve health. However, some of this new progress in healthcare technology is yet to be realised since devices are often ex-

pensive, large or simply provide static readings. Furthermore, portability and wearability play an important role for patients comfort and the modern busy lifestyle. The constant monitoring of body parameters such as humidity and pH in body fluids can be of help to improve treatments that will result in faster recovery and improved health.

Fibre optic technology using optical fibre sensors (OFS) offers a new approach to overcome the limitations mentioned above. The aim of this project is to develop the field of OFS in monitoring parameters such as humidity and pH for the benefit of patients in terms of comfort and accuracy. With regards to the users such as clinicians the OFS potentially provides additional information for better treatments and opens up the possibility of prevention of unnecessary interventions.

The specific objectives of this PhD thesis are listed below:

- 1) To define the humidity and pH monitoring issues found in:
 - 1.1: Wound management
 - 1.2: Newborn delivery and
 - 1.3: Body response during sport performance.
- 2) To provide a background into the OFS technology namely: a brief description of fibre optic properties; sensing techniques; and evaluation systems.
- 3) To review humidity and pH OFS developed to date and compare their novelty, advantages, limitations and potential uses in healthcare.
- 4) To develop a low-cost non-invasive OFS to measure in real-time relative humidity (RH) and to investigate whether it can be embedded within textiles to monitor humidity on the skin.

- 5) To develop an OFS to provide pH measurements within a range of 6.5 - 7.5 pH to provide another approach that can be used in foetal blood sampling (FBS).
- 6) To design a low-cost portable electronic unit to evaluate and characterize the OFS response.

1.8 Motivation

Healthcare in-vivo measurements require devices with small size and hence miniaturization of the sensors is crucial. In the case of wound healing a moist environment is required on the wound surface as explained in Section 1.2. Several devices exist to measure humidity [8], however many of them are either expensive or not suitable to be embedded within wound dressings. Previous research has incorporated electrochemical sensors into such dressings [140, 141, 142, 143] but OFS devices have not yet been widely investigated in such a setting [144, 145, 146, 147]. The OFS potentially offers a more convenient and reliable alternative method of monitoring humidity [78, 125] as it has low-cost fabrication, small size and diameter (micrometres), fast response and high sensitivity [148].

A wound dressing that remotely monitors parameters associated with healing such as humidity present in the wound microenvironment and wound exudate pH could have a significant impact on health care costs [37]. The information obtained from monitoring the wound may be used as a guide to adopt a more accurate management strategy to achieve healing in a shorter time and reduce the number of clinical appointments [23, 149].

In the case of pH measurements, glass membrane electrodes or pH test strips (litmus paper) are commonly used. While glass electrodes are large in size, breakable and unstable over time, pH test strips are an inaccurate sensor with a static measurement. These limitations have motivated the development of new sensors such as OFS which overcome the mentioned barriers [9, 150]. Additional to this, OFS

are safer for in-vivo applications since they do not use electrical currents to work, are not affected by electromagnetic fields (for instance, OFS can be used while doing a magnetic resonance imaging (MRI)) and can contain sensitive films with a strong attachment to the fibre surface.

Moreover, the development of a humidity and a pH sensor that can be embedded within textiles can be extrapolated to the sports field. There is an growing tendency to use wearable sensors to analyse body response under stress and thus improve exercise routines and body recovery. The OFS implementation in garments can be useful to enhance the set of parameters measured such as heart rate and blood oxygenation during sport activities [55]. As explained in Section 1.4, sweat analysis can provide important information to personalise treatments to benefit athletes, reducing potential injuries and thus improve performance.

1.9 Thesis overview

This thesis is divided into six chapters that describe the introduction to the work, literature review, the development of a humidity and a pH sensor based on optical fibre technology and the miniaturization of the evaluation system for real applications in healthcare and sport activities.

Chapter 1, as described above, explains the background of this work: the current problems in wound care monitoring, newborn delivery and sports performance analysis as application fields for the implementation of OFS technology. Special attention is focused on the importance of monitoring humidity and pH. An introduction to OFS is also provided. The objectives and motivations of using OFS to provide a different monitoring approach are defined in this chapter.

Chapter 2 contains the literature review of this thesis. A review of the current OFS developed for humidity and pH monitoring in different applications is described. A comparison among the pros and cons and potential applications of the literature review is provided to show the novelty of the work developed in the following chapters.

Chapter 3 describes the fabrication and performance of the polymeric optical fibre humidity sensor (POFHS) developed. The results of in-vitro and in-vivo tests are shown providing discussion about the comparison with the sensors reviewed in Chapter 2. The POFHS response when embedding within a textile is also studied.

Chapter 4 shows the protocol for the development of an optical fibre pH sensor. The response of the sensor developed for a narrow pH range is compared with a commercial pH meter. An explanation of the potential application of this sensor and the novelty compared with the literature review is also discussed in this chapter.

Chapter 5 reports on the design of a portable cost-effective electronic unit to evaluate the OFS signal and replace the evaluation system used in the laboratory. Moreover, the optical system performance under in-vivo test is shown in this chapter.

Chapter 6 provides an overall discussion and conclusion of the presented work and the future work of the OFSs developed for healthcare and sports applications.

Chapter 2

Literature Review

"Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less."

- Marie Curie -

2.1 Introduction

In this project the implementation of optical fibre sensing technology is proposed as an alternative to the current techniques and devices used to monitor humidity and pH in healthcare and sports applications. In specific for wound healing monitoring, during foetal blood sampling (FBS) procedure and in sport activities.

In the case of wound monitoring, there exists a wide range of dressings including elements such as hydrogels, hydrocolloids and alginates which helps to maintain moisture within the wound area or to absorb wound exudate excess [151]. However, the evaluation of the actual moisture inside the wound is limited. Moreover, the selection of the type of dressing is crucial since an improper choice can disturb the wound healing [152].

On the other hand, another approach to monitor moisture in the wound bed is the impedance measurement of the dressing. It has been studied that the impedance increases as the dressing is in contact with the wound exudate providing clinicians with an insight of the moisture level inside the wound [153, 154]. One of the most commercially used sensors for monitoring wound moisture is the WoundSense sensor (Ohmedics Ltd., Glasgow, UK). This disposable sensor is suitable to be located underneath the dressing. Impedance measurements can be observed in a hand-held meter through a five-stage scale which shows the wound moisture level [155, 156].

In the case of pH monitoring during FBS procedure, the most common technique to collect a blood sample from the newborn consists of the insertion of an amnioscope into the cervix to observe the foetal scalp. An angled blade is inserted into the amnioscope to proceed with the scalp puncture. A sample of blood is collected with a capillary tube to be analysed with a blood gas analyser (BGA). Limitations of this technique are the collection of poor quality samples due to air gaps or blood clots within the capillary tube which results in the repetition of the whole procedure. In addition, the BGA machine is often located in a separate room which can delay the decision taken by clinicians. [53].

Another method used in the delivery suite consists of the location of the umbilical cord insertion on the placenta by ultrasound sector scanner to insert a 20-gauge spinal needle (10 to 13cm long) to collect a blood sample. This less invasive technique produces samples without maternal contamination [157]. However, there exist the risk of abscess formation and haemorrhage in the puncture area in both methods [158, 159].

In the case of body monitoring in sport activities, there exists a series of wearable sensors to monitor blood pressure, heart and respiratory rates [160]. Moreover, biochemical sensors for sweat composition analysis (for example, pH and sodium) have been widely studied [161, 162]. However, there exists a limited application of such wearable sensors for sweat rate evaluation. The capacitive humidity sensors have been currently implemented in sportswear due to the sensor size and the simple circuitry required. Sweat rate measurements are based on the difference in the response of two capacity humidity sensors located at different heights from the skin. In this case, the sensitivity is limited by the distance in the location of the sensors. Measurements can be compared with a Vapometer (an instrument used for evaporation rate measurements) [163, 164].

This chapter presents a literature review of the optical fibre sensors for humidity and pH measurements developed to date. Several characteristics will be highlighted in this chapter namely: the geometrical configuration of the sensor; the sensitive film deposited onto the optical fibre; the followed coating method; the sensitivity range detected; and the sensor response time.

These parameters will introduce information for a comparison between their advantages and limitations, thereby illustrating the novelty of the work developed in this PhD for healthcare and sports applications.

2.2 Optical fibre humidity sensors review

In Chapter 1, the importance for monitoring humidity in healthcare and sports applications was described. In addition, the limitations of the current techniques

to monitor humidity in these fields (for example, unsuitability for in-vivo applications) have been a stimulus for the expansion of the fibre optic sensor technology.

In this section, a chronological review of some of the relevant optical fibre sensors for relative humidity (RH) measurements is presented. Special attention will be given to certain characteristics, for example the geometrical configuration of the fibre, the principle of operation, the humidity range detected and the response time of the sensor. The reviewed sensors are mainly based on the evaluation of the attenuation of light due to the interaction of the sensitive coatings with the surrounding environment.

Ogawa et al. way back in 1988 [165] reported the humidity response of a microporous SiO_2 cladding covering the surface of a silica core fibre optic cable. Unfortunately the coating method was not reported. Results showed a decrease in the transmitted power as the RH increased in a range of $\sim 20\%$ - $\sim 95\%$ with a detection error of $\pm 5\%$ and a response time of 15s. Variation of temperature with constant RH was evaluated resulting in a variation of 0.1dB in optical power which is not significant for the total measurement.

A couple of years later, in 1990 Muto et al. [166] developed a moisture-sensitive plastic optical fibre for monitoring atmospheric humidity and moisture equivalent in the soil. The central region of the exposed fibre core (1mm diameter) was spin-coated with phenol-red (PR) which is a dye whose absorption coefficient at a wavelength of $\sim 530\text{nm}$ changes according to the moisture in the environment. The film thickness was about $1\mu\text{m}$. A reversible response was observed at the range of 30% - 50% RH. The influence of temperature had no significant changes on the sensor behaviour. The response time measured was $< 10\text{s}$.

In 1995, Kharaz et al. [167] developed an intrinsic optical fibre humidity sensor (OFHS) based on the colorimetric interaction of cobalt chloride (CoCl_2) with water molecules. The sensitive cobalt chloride gelatin thin film was immobilised onto the exposed core region (50mm length) of a multi-mode optical fibre with $600\mu\text{m}$ core diameter. Attenuation of light was observed in the wavelength region

of 600nm - 740nm over relative humidity variations. A second wavelength outside these regions was monitored as a reference for light intensity variations caused by additional parameters such as temperature. The sensor operating regions were found at 0% - 40% RH, 40% - 70% RH and 70% - 100% RH with a sensitivity of 0.001, 0.007 and 0.002 in relative intensity units per percentage of relative humidity, respectively. The response time achieved was ~ 1 s.

Arregui et al. in 1999 [121] developed a humidity sensor using a different sensing and fabrication method. To create the sensor a single-mode optical fibre was coated with a novel method named ionic self-assembly monolayer (ISAM). This method consists of the alternate deposition of cationic and anionic polymers, similar to the layer-by-layer (LbL) technique. The anionic solution was poly(sodium 4-styrene-sulfonate) salt (PSS) whereas a solution of gold colloids protected by poly(diallyldimethyl ammonium chloride) (PDDA) produced a cationic solution (Au:PDDA). Following the ISAM method, a number of bilayers were coated on the tip of the fibre. The layer structure forms an interferometric cavity, hence, the sensor operates as a Fabry-Perot etalon. The largest variation in reflected optical power (4.77dB) was observed after coating 65 bilayers for a RH range of 11.3% - 85%. The thickness of each layer measured by an ellipsometer in a flat substrate was ~ 4.75 nm, therefore the length of the nano Fabry-Perot cavity was ~ 309 nm. Response time over sudden RH changes was < 1.5 s, hence the sensor can be used for breath monitoring.

In the next year, 2000, Barriain et al. [168] developed a humidity sensor based on a biconically tapered fiber coated with agarose gel. A single-mode fiber ($9.84\mu\text{m}$ and $125\mu\text{m}$ core and cladding diameter, respectively) was stretched with an electric splicing unit to produce a waist diameter of $25\mu\text{m}$. Agarose, which is considered a biopolymer originating from marine algae with hydrophilic properties, was dissolved in water to produce a gel. This gel was deposited on the tapered region of the fibre. The sensing mechanism relies on the attenuation of light produced by the humidity-induced refractive index variation in the agarose gel. A linear and reversible response was observed in the range of 30% - 80% RH. Moreover, the response and recovery time recorded over a 10s long breath (to provide a

sudden humidity change) was 5s and 55s, respectively. Therefore, this sensor is not suitable for breath monitoring.

On the basis of the work developed in [166], Gupta et al. in 2001 [169] produced a humidity sensor using a plastic-clad silica (PCS) fibre coated with a phenol red doped polymethyl methacrylate (PMMA) film by dip-coating at a speed of 10cm/min. Moreover the sensor has a "U" structure (2.45mm bending radius) due to the increased evanescent wave (EW) field absorption. The operational range of the sensor was 20% - 80% RH with a response time of ~ 5 s. Further studies were made for U-shape sensors with larger bending radius, but it was observed that as the bending radius decreases the sensitivity increases. This effect is explained because of the reduction of angle of incidence light at the core-film interface which increases the interaction with the film and hence the absorption.

In 2002, Jindal et al. [170] fabricated two OFHSs with different geometrical configuration (straight and U-shape) using multi-mode optical fibre (200 μ m core diameter). Both sensors were coated with a humidity sensitive film based on polyvinyl alcohol (PVA) and CoCl_2 by dip-coating method. The principle of operation is based on the attenuation of light due to the interaction of the EW and the sensitive film with the environment. Measurements were taken at 632.8nm wavelength, however an optimum performance of the sensor can be achieved using a wavelength of ~ 690 nm since the CoCl_2 has a strong absorption around this wavelength. The straight sensor (PVA/ CoCl_2 film deposited onto the unclad central portion of the fibre) registered only humidity variations above 78% RH. In order to increase the humidity range and the EW interaction with the film a bent fibre was also fabricated. The U-shape was formed by manually bending the fibre while heating the bare core on a propane flame. Unfortunately, details about the bending radius and the response time of each sensor are not reported. In this case, the operative region was increased from 3% - 90% RH.

Muto et al. [171], in 2003, also studied the humidity response of a plastic optical fibre (POF) coated with a film of hydroxyethylcellulose (HEC) and polyvinylidene fluoride (PVDF). The selection of the film components was due to its refrac-

tive index change compared to humid air. The sensor was fabricated by coating the HEC/PVDF film on the fibre core made of PMMA. The refractive index of the coating is slightly higher than the refractive index of the core, therefore, under dry environments the fibre operates as a leaky-type sensor. However, with exposure to humid air, the film refractive index decreases and it becomes lower than the core refractive index, thus the sensor acts as a waveguide. The experimental results confirmed the sensing properties of the film over a RH range of 50% - 70% with a response time of ~ 2 s. In addition, the sensor shows repeatability and almost no dependence with temperature changes since its operation principle depends on the core-cladding refractive index changes. The fast response time meant that the sensor could be used as a real-time breathing monitor.

In 2004, Gaston et al. [172] developed a humidity sensor based on a side-polished single-mode optical fibre. The use of hygroscopic macromolecular polymers (hydrogels) was studied. Solutions containing 3 wt.% PVA in distilled water were prepared to coat the fibre. The dissolved material was placed on the surface of the polished region by dip-coating method. Exposure to water produces swelling in the PVA film due to the formation of hydrogen bonds, hence the refractive index of the coating is decreased and optical power losses are registered. The sensor recorded a linear response in the humidity range of 72% - 87% with a sensitivity of 0.53dB/% RH. In addition, breath pulses were expelled over the sensor. The response time observed was < 1 min.

Moreover, in 2004, Xu et al. [173] presented an OFHS based on EW scattering. A bent fibre was used since the EW is stronger compared with a straight fibre. The U-shape was produced by burning off the cladding of the central portion of the fibre. The silica core surface was then activated with NaOH to be dip-coated with a porous sol-gel silica (PSGS) based on TMOS. A wide range of wavelengths was monitored to select the optimum evaluation wavelength. Light in the near-infrared (NIR) range was chosen for measurements. The sensor showed a logarithmic response as the humidity was increased in the range of 3% - 89% with a response time of ~ 5 s.

The humidity sensor produced by Khijwania et al. in 2005 [78] consists on a PCS fibre with a humidity sensitive film deposited in the central section of the fibre where the core was exposed. The absorption of the EW in the sensitive region was measured as the humidity was modified. In order to enhance the interaction of the sensor with the environment, the fibre was bent into a U-shape with a bending radius of 5mm. This will produce light to pass from guided modes to leaky modes, thus more interaction with the analyte will result compared with a straight sensor where the length of the sensitive region will define the sensitivity. Studies were made to calculate the penetration depth of the EW and therefore the film thickness necessary to obtain maximum sensitivity. The film coated was based on PVA and CoCl_2 by dip-coating. Results showed that 2 dip-coatings were more sensitive in the range of 20% - 92% RH. Further increase of film thickness reduced sensitivity since the film was thicker than the penetration depth of EW, hence, even though there was a film with higher concentration, the analyte does not interact with EW. It was observed that the film absorbs more light in dry environments and vice versa.

Zhao et al. in 2011 [174] developed two OFHSs based on EW absorption. A multi-mode fibre was manually bent using a flame until reaching a "U" structure to enhance EW penetration depth and thus interaction with the sensitive film. Two bending diameters were studied, 1.5cm and 0.5cm. Prior to bending, the cladding from the central portion of the fibres was removed. The sol-gel technique was used to coat the unclad section of the fibres by dip-coating at 0.3mm.s^{-1} . TEOS and methylene blue were used as precursor and indicator, respectively. Absorbance measurements were monitored for both sensors using a set of flowmeters which provided different values of RH. A logarithmic linear relationship with RH was observed with both sensors over the range of 1.1% - 70%, RH. It was found that the 1.5cm U-shape recorded higher absorption. However, for a low RH range of 1% - 4.5% a linear and more sensitive response was obtained compared with RH range of 50% to 70%. The response and recovery times of 20s and 25s, respectively were found. Increasing the RH range to 16.2% increases the response and recovery times to 30s and 3min, respectively.

A year later, in 2012 Mathew et al. [175] developed a humidity sensor based on a single-mode optical fibre under U-shape geometrical configuration. A high bend loss fibre (1060XP, Thorlabs Ltd.) was used to increase bending radius and reduce risk of fibre breakage. The bending radius was 16.75mm. The U-shape was coated by dip-coating method with agarose providing a sensitive range of 25% - 90% RH and a response time of 0.5s. The humidity sensitivity of the sensor is wavelength dependent. Higher transmission loss, i.e. sensitivity with respect to humidity was observed at higher wavelengths (5dB transmission loss at 1600nm for a change in relative humidity of 65%). Repeatability in measurements was observed for a humidity cycling in the range of 60% - 80%RH.

In 2015, Harith et al. [176] created a humidity sensor using a POF (1mm diameter). The fibre core was exposed in the central section of the fibre (10mm length) by chemical etching technique using acetone until a diameter of 0.45mm was reached. An Al-doped ZnO nanostructure (1 mol% concentration) was prepared by sol-gel method. The fibre was immersed into the solution for 15hrs. A linear response over a humidity range of 50% - 80% was observed with a sensitivity of 0.0172mV/%RH. Unfortunately, the response time of the sensor was not reported.

Table 2.1: Optical fibre humidity sensors review.

Author	Reference & year	Geometrical configuration	Sensitive film	Humidity range	Response time
Ogawa et al.	[165], 1988	straight	SiO ₂	~20% - ~95%	15 s
Muto et al.	[166], 1990	straight	PR	30% - 50%	<10 s
Kharaz et al.	[167], 1995	straight	CoCl ₂	0% - 100%	~1 s
Arregui et al.	[121], 1999	fibre tip	PSS/Au:PDPA	11.3% - 85%	<1.5 s
Bariain et al.	[168], 2000	tapered fibre	Agarose	30% - 80%	<5 s
Gupta et al.	[169], 2001	U-shape	PR	20% - 80%	~5 s
Jindal et al.	[170], 2002	straight U-shape	PVA/CoCl ₂	>78% 3% - 90%	-
Muto et al.	[171], 2003	straight	HEC/PVDF	50% - 70%	~2 s
Gaston et al.	[172], 2004	side-polished	PVA	72% - 87%	<1 min
Xu et al.	[173], 2004	U-shape	PSGS/TMOS	3% - 89%	~5 s
Khijwania et al.	[78], 2005	U-shape	PVA/CoCl ₂	20% - 92.39%	~1 s
Zhao et al.	[174], 2011	U-shape	TEOS/Methylene blue	1.1% - 70%	~20 s
Mathew et al.	[175], 2012	U-shape	Agarose	25% - 90%	0.5 s
Harith et al.	[176], 2015	Straight	Al-doped ZnO	50% - 80%	-

Table 2.1 summarises the main characteristics of the optical fibre humidity sensors listed in the literature review. The principle of operation most commonly found in the sensors is based on the interaction between the EW of the fibre and the film coating with the environment. Moreover, the film refractive index plays an important role since its modification due to the humidity in the environment produces light attenuation which can be recorded.

On the other hand, it can be noticed that most of the sensors reported a fast response time ($<5s$) for a wide RH range. The sensor geometrical configuration is independent of the sensitivity since similar humidity range was observed with the straight and U-shape sensors. However, the U-shape can only be produced in fibres with silica core due to the use of a flame to burn the plastic cladding.

In Section 2.4 the novelty of the optical fibre humidity sensor developed in this PhD over the properties of the introduced sensors will be explained.

2.3 Optical fibre pH sensors review

Currently, there exists a wide range of pH sensors developed, including sensors based on optical fibre technology. This section presents details of the optical fibre pH sensors developed to date along with a review of the techniques used for fabrication and its application. The fibre optic pH sensors reported are based on the immobilization of a sensitive dye onto an unclad section of the fibre. Techniques such as LbL and sol-gel were found as the most commonly used. An important characteristic of the coating technique used is that the dye must not leach out of the fibre to prevent any inflammatory reactions for in-vivo measurements as defined in the Biocompatibility standard ISO 10993.

The fibre optic pH sensor produced by Ge et al. [177] in 1993 is based on the EW absorption of an immobilized conductive polymer (polyaniline). A multi-mode optical fibre with 10cm of cladding removed on the middle section of the fibre was used. The cladding was replaced with a synthesized polyaniline film with a concentration of 0.5M. Details about the coating technique were not provided. Near-infrared (NIR) light was launched into the fibre to detect the absorption

according to the pH of the test solution. A set of 32 wavelengths from 1100 to 1450nm were measured with a separation of 11nm per wavelength. The pH range tested was from 3 - 12, pH level. The pH measurements were constrained to this range in order to avoid damaging the sensitive film. The largest absorption was observed at 1428nm. For pH ranges of 3 - 5.5 and 8 - 12 the absorption change was very small, however for pH from 6 - 8, the absorbance changed significantly. The response time was 4min due to the film thickness, however, it is expected to reduce this response time by coating the core with a thinner polymer film.

In 1997, Gupta et al. [178] developed a set of optical fibre pH sensors based on EW absorption. The sensors consisted of three plastic-clad silica (PCS) fibres with 5cm of cladding removed in the middle section and subsequently coated with a pH sensitive film following the sol-gel technique. TEOS was used as the precursor for all the fibres due to the lower refractive index than that from the core, thus allowing TIR. Dye compounds such as phenol red (PSP), cresol red (CR) and bromophenol blue (BPB) were used as indicators for each fibre. The fibres were dip-coated at a withdrawal speed of 10cm/min producing a film thickness of 0.15 μ m. The operating wavelength where higher absorption was recorded was 620nm for all the sensors. Results showed: a dynamic range of 7.5 - 11.5 pH for the sensor based on PSP; 6.5 - 11 pH for the sensor with CR; and 4.0 - 7.5 pH for the case of the sensor with BPB. Response time was calculated for a step change from 7 - 12 pH. A response time of $\sim$ 5s was obtained in all the sensors.

In the same year, Grant et al. [131] developed an OFS for pH measurements on human blood. This sensor was fabricated using the sol-gel technique to entrap seminaphthorhodamine-1 carboxylate (SNARF-1C) as a pH indicator with a pK_a of 7.4, ideal for pH measurements in blood. Tetramethyl orthosilicate (TMOS) and phosphate buffered saline (PBS) were used as reagents. The tip of a multi-mode silica optical fibre was dip-coated into the sol-gel solution. The sensing technique is based on ratiometric measurements of two different wavelengths. The pH is calculated by evaluating the peak emission intensity ratio of either the acid or base form (580nm and 640nm for this pH indicator, respectively) and the isosbestic point at approximately 610nm. The sensor has a linear

and reproducible response in the range of 6.8 - 8.0 pH with a response time of 15s and low leachability ($\sim 7\%$ after 1 month) making it suitable to be used within an array of catheter-based microtools. The applications of this sensor was for the development of an array of sensors to monitor stroke patients.

Gupta et al. [179] produced another pH sensor in 1998. The fabrication, optical fibre and sensing method were the same as their previous work [178]. The difference was the pH indicator, which in this case was a mixture of three dyes: CR, BPB and chlorophenol blue (CPB) to cover a pH range of 8.5 - 13. The operating wavelength was found at 600nm. A linear variation can be observed for the range of 4.5 - 13 pH with reproducible results. Response time was ~ 5 s.

Few years later in 2001, Gupta and Sharma [180] developed a pH sensor based on a U-shaped probe. The sensitive film based on CR, BPB and CPR was produced and coated on the core as explained in [179] in order to provide the sensor with a wide pH sensitive range. Three probes with different bending radii (3.48mm, 1.14mm and 0.82mm) were fabricated using PCS fibres. Higher sensitivity was observed with the sensor at a 0.82mm bending radius where 80% of the transmitted power was absorbed compared with 50% recorded in the straight sensor developed previously [179]. In addition, the effect of the numerical aperture (NA) on the sensitivity was studied, where it was found that a higher NA increased the sensitivity. The calibration curve was obtained for the range of 4 - 9. The response time for a sudden increase in pH was 15s.

Also in 2001, Lee et al. [10] presented a new approach to enhance the sensitivity of pH indicator films. This new proposed method consisted of a multiple sol-gel technique where different layers of sol-gel containing the indicator were coated successively one on top of each other. The fibre used was a multi-mode PCS with 5cm of cladding removed in the central region of the total length of the fibre. TEOS is used as a precursor whereas Bromocresol purple (BCP) and bromocresol green (BCG) were used as indicators for the sol-gel preparation. The fibre was dip-coated at 100mm/min producing a ~ 200 nm thick film. After a complete curing of the film, a second layer is coated on the top, this process is repeated

to obtain an interface between layers. Measurements of BCP and BCG shows similar absorbance in the acidic and alkaline form of the spectra. The relationship between penetration depth of EW and the film thickness was studied. One way to deposit thicker films was by increasing the withdrawal rate of the dip-coating, however, this conveys fragility to the film and hence cracks appear on the coating. The new method of multiple sol-gel coatings counter-acts this issue since the different layer interface provides a buffer layer and avoids cracking the film. Moreover, it was observed that an increase in sensitivity occurred as the layers were increased. Nonetheless, the number of layers and hence its thickness is limited by the penetration depth of EW. The pH range obtained for the sensor coated with BCP was 7.5 - 10.5, whereas the sensor coated with BCG reported a pH range of 6.5 - 9.5. The response time in both sensors was of 5s for an increment in pH. Conversely, when the pH decreases, the response time recorded was 30s.

Miled et al. [181] in 2002 created an optical fibre pH sensor based on a dye doped mesostructured silica. TEOS was used as precursor whereas thymol blue (TB) was used as the pH indicator. The silica core of a multi-mode optical fibre was exposed in the middle section of the fibre (3cm length). The film coating was performed by putting a drop of the sol-gel on the unclad fibre section and shifting it from one side to the other until a uniform film of about $5\mu\text{m}$ thickness was formed. The absorption of the EW was recorded to obtain the sensor response. The dynamic response of the sensor was found in the range of 3.8 - 12.3 pH. However, reversibility can only be observed in a narrow range pH range of 8 - 12. The recorded response time was $\sim 5\text{s}$.

In the same year, Lee et al. [120] presented a different approach for a fibre optic pH sensor by demonstrating the effect of microbending the fibre to enhance the EW field instead of exposing the fibre core. To produce a microbend, the fibre was placed between a pair of corrugated plates where pressure was applied with a pitch of 1mm. The microbend region was coated with a sol-gel solution based on TEOS as the precursor and a mixture of dyes such as BCP, BCG and CR as indicators to provide a broad range of pH measurements. Dip-coating technique

was performed at a withdrawal rate of 100mm/min. The evaluated absorption wavelength was 633nm. The dynamic range of the sensor was 3 - 11 pH. The advantage of this sensor is the reproducibility since chemical etching is not required.

In 2003, Gaston et al. [102] developed pH sensor based on a single-mode fibre. The fibre was side-polished on the central portion of the fibre. Sol-gel method was followed to cover the polished section by dip-coating technique. TEOS was used as a precursor whereas a pH-sensitive dye namely Eriochrome cyanine R (ECR) was used as indicator. Absorbance measurements of the spectra were taken at 635nm obtaining a high sensitivity for the pH range of 9 - 12. Unfortunately details about the response time are not described.

Another work presented by Miled et al. [182] few years later in 2004, reported a sensor fabricated with the same configuration (straight sensor), but with a different sensitive film coated onto the exposed core. Precursors used for the sol-gel formation were TEOS and cetyltrimethylammonium bromide (CTAB), whereas bromothymol blue (BTB) was used as the pH indicator. The film was coated onto the unclad section of the fibre (3cm length) by dip-coating method at 3.1mm s^{-1} withdrawal rate to obtain a film thickness of $\sim 1.5\mu\text{m}$. The optical fibre was heat treated at 150°C to harden the film. The EW method was followed to observe the sensor response to pH modification. Higher sensitivity was observed in the acidic region (2 - 5 pH) rather than the alkaline range where no significant changes in transmittance were noticed. Unfortunately, reversibility was an issue with this sensor and response time is not reported.

The work presented by Beltran-Perez et al. [133] in 2006 is based on the fabrication of an optical fibre pH sensor where TiO_2 is used as a supporting matrix for the sol-gel solution. The pH indicators selected were brilliant green (BG), rhodamine 6G (R6G), rhodamine B (RB) and coumarin (CM). The unclad portion ($\sim 6\text{cm}$) of a multi-mode optical fibre was dip-coated into the sol-gel solution. To test the pH response of the sensor, the fibre was submerged in a solution that continuously changes its pH by adding acid or base chemicals such as KOH and HNO_3 , respectively and agitating the solution with a magnetic stirrer. The opti-

cal power output was observed for fibre sensors with one of the dye compounds entrapped with TiO_2 . The most sensitive film was the combinations of TiO_2 :CM and TiO_2 :R6G given a pH dynamic range of 2 - 5.5 and 6.5 - 11, respectively. Measurements at 400nm produced the highest sensitivity. In addition, the effect of TiO_2 as a supporting matrix provides the sensor with a long life time (~ 8 months).

Dong et al. [132] in 2007 fabricated a broad range optical fibre pH sensor by adding a set of indicators to the sol-gel coating. The middle section of the fibre was unclad by chemical etching using hydrofluoric acid (HF) (4cm length). The multi-mode fibre was treated with 30% HNO_3 to activate the OH groups on the unclad surface to improve the adhesion of the film. TEOS was used as a precursor and Triton X-100, which is a surface active reagent, was added to reduce cracks on the sol-gel film. The fibre coating was performed by placing a drop of the silica sol on the unclad section of the fibre and moving it from side to side until a uniform film was observed. The entrapped indicators were CR, BPB and CPR. The optical power of the sensor was measured to observe the pH response which was almost linear in the range of 4.5 - 13 with a response time of ~ 5 s. No significant readings were obtained for pH values lower than 4.5, whereas for pH above 13 the film presented cracks and partial removal. In this work, special attention is given to the performance of Triton X-100 in the sol-gel solution. It was observed that the surface active reagent improved the sensitivity, reversibility and robustness of the sensor.

One year later, in 2008 Goicoechea et al. [123] evaluated the colorimetric response of neutral red (NR) deposited onto an optical fibre with respect to pH. To coat the indicator, LbL method was followed. Poly(acrylic acid) (PAA) was used as the polyanion. The cladding from the tip of a multi-mode PCS fibre was removed by chemical etching using acetone. Silver paint was spread at the end of the fibre to produce a mirror. The number of NR/PAA bilayers deposited was 15. Reflection measurements were undertaken since light passes twice through the sensing region, therefore, more sensitivity can be obtained. The spectral response showed a peak at 480nm that changes proportionally to the pH and a

valley at 650nm changing in the opposite direction. Difference of both absorption values were calculated to obtain the pH measurement. Response time and resolution recorded were ~ 1 s and 0.03 pH units, respectively. Hysteresis was observed in the range of 5 - 8 pH with a maximum value of 13.5% of the total dynamic range. Repeatability of the sensor can be obtained for a pH range of 3 - 9 and cross-sensitivity to temperature has a low effect on the output signal.

Raoufi et al. [122] in 2014 demonstrated the design of an optical fibre pH sensor probe using the LbL coating method. The film deposited onto the fibre core consisted on bilayers of poly(allylamine hydrochloride) (PAH) and brilliant yellow (BY), the latter being the pH indicator. Two different sensor shapes were prepared: a straight sensor and a U-shape sensor. In the former, the film was deposited on one end of the fibre where a mirror was also created to reflect light back to the other end of the fibre to be evaluated. In the latter sensor, the fibre was manually bent using a flame to obtain the U-shape. Cladding was removed prior to coating of the sensitive regions. Several factors were changed to optimize the sensor response such as core diameter ($600\mu\text{m}$ and $1000\mu\text{m}$), concentration of the indicator (0.25mM and 0.5mM), number of bilayers (3 to 9), outer layer of the film (PAH or BY), and radii of the U-bend (1.15mm and 1.55mm). After testing the probes it was concluded that 5 to 6 bilayers was the optimum and increasing further the number of layers reduced the sensitivity. In addition it was observed that the U-shaped sensor with a small bending radius has increased sensitivity. Lower indicator concentration and larger core diameters also enhanced the sensitivity for over a narrow pH range (7 - 9) for both the straight and the U-shape optical fibre sensors.

Table 2.2: Optical fibre pH sensors review.

Author	Reference & year	Geometrical configuration	pH indicator	pH range	Response time
Ge et al.	[177], 1993	straight	polyaniline	6 - 8	4 min
Gupta et al.	[178], 1997	straight	PSP CR BPB	7.5 - 11.5 6.5 - 11 4 - 7.5	5 s
Grant et al.	[131], 1997	fibre tip	SNARF-1C	6.8 - 8.0	15 s
Gupta et al.	[179], 1998	straight	CR-BPB-CPB	4.5 - 13	~5 s
Gupta and Sharma	[180], 2001	U-shape	CR-BPB-CPR	4 - 9	15 s
Lee et al.	[10], 2001	straight	BCP BCG	7.5 - 10.5 6.5 - 9.5	5 - 30 s
Miled et al.	[181], 2002	straight	TB	8 - 12	~5 s
Lee et al.	[120], 2002	microbend	BCP-BCG-CR	3 - 11	-
Gaston et al.	[102], 2003	side-polished	ECR	9 - 12	-
Miled et al.	[182], 2004	straight	BTB	2 - 5	-
Beltran-Perez et al.	[133], 2006	straight	BG-R6G-RB-CM	2 - 12	-
Dong et al.	[132], 2007	straight	CR-BPB-CPR	4.5 - 13	~5 s
Goicoechea et al.	[123], 2008	fibre tip	NR	3 - 9	~1 s
Raoufi et al.	[122], 2014	fibre tip U-shape	BY	7 - 9	-

Table 2.2 points out the main characteristics of the optical fibre pH sensors reviewed in Section 2.3. It can be noticed a trend for the use of dye compounds as pH indicators. These indicators can be easily immobilized onto the core surface by sol-gel means since this technique can be performed at low temperatures, hence the dye properties are not compromised. In addition, although some dyes are more sensitive to a certain pH range, two or more dyes can be mixed in order to widen the dynamic pH range of the sensor. Dip-coating was found as the most commonly used method for film deposition since the film thickness can be controlled with respect to the withdrawal speed.

On the other hand, as mentioned in [181], the reversibility of measurements and the response time are also important factors to consider for the pH sensing with optical fibres. The next section will explain the novelty behind the optical pH sensor developed in this PhD compared with the characteristics of the inspected sensors.

2.4 Novelty of the work developed in this PhD

An increasing trend has been shown for the fabrication of OFSs for humidity and pH measurements. The OFSs presented used either LbL technique or sol-gel method to entrap a sensitive element onto the fibre core. Moreover, advantages such as fast response, reversibility, durability and increased signal to noise ratio (SNR) compared with commercial sensors were reported.

As presented in Chapter 1, there is an increasing demand to provide new approaches for humidity and pH measurements in healthcare, specifically for wound monitoring, newborn delivery and body response during sports. Applications of OFS have yet to be increased in order to cover the healthcare applications mentioned. Most of the sensors found in the literature review are not used for these purposes, few of them are used for respiratory monitoring and blood pH measurements. For that reason, the novelty of the sensors developed in this PhD are described in the following paragraphs.

The humidity sensor developed in this work was coated with a hydrophilic film

based on SiO_2 nanoparticles by LbL method. Contrary to the literature review, the fibre used for the humidity sensor has both cladding and core made of plastic in order to facilitate the integration within textiles. As described by [144, 145, 146], OFHS have not yet been investigated within textiles. In Chapter 3, the response of the polymeric optical fibre humidity sensor (POFHS) developed is observed after embedding the sensor within a textile and measuring the humidity from the skin. This work provided promising results for the implementation in wound dressings for wound care or in garments to monitor humidity on the body during sporting activities. In addition, the POFHS performance was tested to measure the humidity response from the body while cycling. The POFHS produced encouraging results to implement the sensor in sportswear and monitor in real-time the humidity expelled from the body during exercise.

In the case of the optical fibre pH sensor, the literature review showed a broad dynamic pH range. Sol-gel coating technique has been proven to be an excellent immobilization technique for dye compounds, resistant to aggressive environments and with low leaching rate. For these reasons, for the pH sensor developed, the sol-gel technique was followed to coat a U-shaped optical fibre. The pH indicator used was tetrakis-(4-sulfophenyl)porphine (TSPP), a dye compound studied for its optical properties which produces two main absorbance bands whose absorption values follows the pH modification. The novelty of the pH sensor developed is the dynamic range which is from ~ 6.7 - ~ 8.1 . In addition to this, the optical fibre pH sensor is capable to measure pH variations within a narrow range as a key feature for potential implementation in medical applications such as foetal blood sampling (FBS), as explained in Section 1.3. Chapter 4 provides more details of the fabrication and performance in real-time of the pH sensor developed in this PhD.

Furthermore, the experimental set-up deployed in the sensors reviewed above for humidity and pH measurements are not practical for in-vivo portable applications. An additional novelty presented in this PhD is the design of a low-cost portable evaluation system that can remotely monitor the resulting signal from the humidity and pH proposed sensors.

2.5 Summary and comments

This chapter has described the current status of the deployment of optical fibre sensors described in the literature for the measurement of humidity and pH.

The areas lacking that this thesis addresses are:

1. Deployment of plastic optical fibre sensors
2. Real time in-vivo humidity measurement
3. Real time in-vivo pH measurement
4. Implementation of a portable evaluation system

The next chapter will describe the polymeric optical fibre sensor deployed in the thesis for humidity measurement.

Chapter 3

Polymeric Optical Fibre Humidity Sensor

"Important thing in science is not so much to obtain new facts as to discover new ways of thinking about them."

- Sir William Bragg -

3.1 Introduction

Humidity measurements are important for several aspects of daily life, such as air conditioning, meteorological forecast and in industrial settings. The level of humidity is quantified by the term relative humidity (RH), which is defined as the ratio of water vapour present in the environment to the maximum amount of water that the environment can hold, expressed as a percentage (%RH). Additionally, moisture is a term also related to humidity, it is considered as water in liquid form found in the surface of solid materials [183].

Depending on the application field different methods for humidity measuring can be employed [8]. Previous research has shown different approaches of humidity sensors based on silica core optical fibre [184, 185, 173]. However, although most of the optical fibres are made of glass, it is known that a silica core fibre may not be suitable for use in a harsh environment due to its fragility after removing the cladding, for example during sport activities.

In contrast, plastic optical fibres (POFs) have advantages such as higher flexibility/elasticity that allows more pressure and strain to be applied onto the fibre to resist rough handling compared with silica fibres [186]. These parameters makes POFs well suited to be reliable for sensing applications [187]. The typical POF refractive indices are 1.5 and 1.4 for the core and cladding, respectively, 0.5 NA and acceptance angle of 30° . Standard POFs have a polymethyl methacrylate (PMMA) core and a cladding made of a polymer with a lower refractive index (commonly fluoropolymer) [188]. POF can be found with diameters from $85\mu\text{m}$ to $3000\mu\text{m}$ [189].

On the other hand, POFs present some disadvantages such as restriction to be fabricated only as multi-mode fibre due to the properties of plastics and higher attenuation that reduces its application field to short distances and temperature limitations ($<85^\circ\text{C}$).

The fabrication and characterisation of a polymeric optical fibre humidity sensor (POFHS) will be described in this chapter. The unclad central region of

the POF was coated by a hydrophilic mesoporous film based on poly(allylamine hydrochloride) (PAH) and SiO₂ mesoporous nanoparticles (PAH/SiO₂) following the layer-by-layer (LbL) deposition method [190]. The principle of operation of the POFHS is based on the measurements of the light intensity changes due to the interaction between the evanescent wave (EW) and the hydrophilic film, which changes its refractive index according to the humidity in the environment.

3.2 Materials and instrumentation

ESKA SK-10 multi-mode POF (1.49 refractive index, 0.5 NA, Mitsubishi Rayon Co., Ltd.) with core diameter of 240 μ m PMMA resin and 5 μ m fluorinated polymer cladding was used. The set-up for the sensor fabrication consists of a tungsten halogen lamp (Ocean Optics HL-2000, wavelength range $\lambda = 360\text{nm} - 2400\text{nm}$), sub-miniature version A (SMA) connectors for each end of the POF which is placed within a holder made of Teflon containing a channel of dimensions 50mm length, 5mm width and 7mm height and a spectrometer to monitor light intensity changes (Ocean Optics USB 2000+, detection range $\lambda = 200\text{nm} - 1100\text{nm}$). The spectrometer is connected to a computer via a USB port in order to control the spectrometer and record the data (Figure 3.1).

3.3 Sensor fabrication

Since the optical fibre sensor developed is based on the EW absorption, the first step is to expose the fibre core by removing the cladding by a chemical etching technique. The mid-section region of the POF is placed in a Teflon holder where acetone ((CH₃)₂CO) is constantly poured for around 25 minutes since the cladding is acetone-soluble. The diameter of the optical fibre after cladding removal was measured using a microscope (BX50F4, Olympus optical Co. Ltd.).

The POF cladding is only 5 μ m thick, hence it can be easily removed. Nonetheless, it was observed that by removing also a small part of the core, a more uniform surface is achieved in order to obtain better film deposition and therefore higher interaction between the EW and the humidity sensitive film. Scanning electron

microscopy (SEM) (Philips (FEI) XL30 FEG ESEM) images from the unclad section of the fibre and after the film deposition on the exposed core were taken to compare the fibre sensing region surface (Figure 3.6). For SEM measurements a sample of the exposed fibre core was coated with platinum (Pt) using the sputtering coating method.

Once the cladding and a part of the core are removed the humidity sensitive film is deposited using the LbL method, following the set-up used for the chemical etching (Figure 3.1).

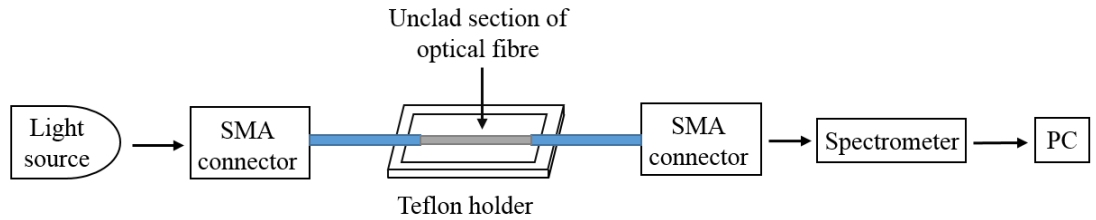


Figure 3.1: Set-up for monitoring the polymeric optical fibre humidity sensor (POFHS) fabrication process.

SiO₂ mesoporous nanoparticles (SNOWTEX 20L, 40-50nm diameter, Nissan Chemical, Japan) were deposited with poly(allylamine hydrochloride) (PAH) to form a PAH/SiO₂ hydrophilic material which creates a higher humidity sensitivity compared with microporous and macroporous materials [191].

The PAH/SiO₂ layers were deposited in three steps as illustrated in Figure 3.2. First, the unclad surface of the POF is placed within the Teflon holder. The core surface is activated by depositing 1wt% ethanolic KOH in order to functionalise it with OH⁻ groups. After 20 min, KOH is removed using an aspiration pump and the fibre is rinsed and dried with deionized water and Nitrogen gas (N₂), respectively.

Second, the fibre is bathed in 0.17wt% of positively charged PAH (Sigma-Aldrich Co, UK, polycation, pH = 11) for 15 min. After the polycation deposition, the fibre is washed and dried again. The third stage is to immerse the fibre in a solution containing negatively charged SiO₂ nanoparticles for 15 min. Then, the

fibre is once again washed and dried to remove any excess nanoparticles and to obtain a uniform monolayer. In order to deposit more layers, the second and the third steps are repeated.

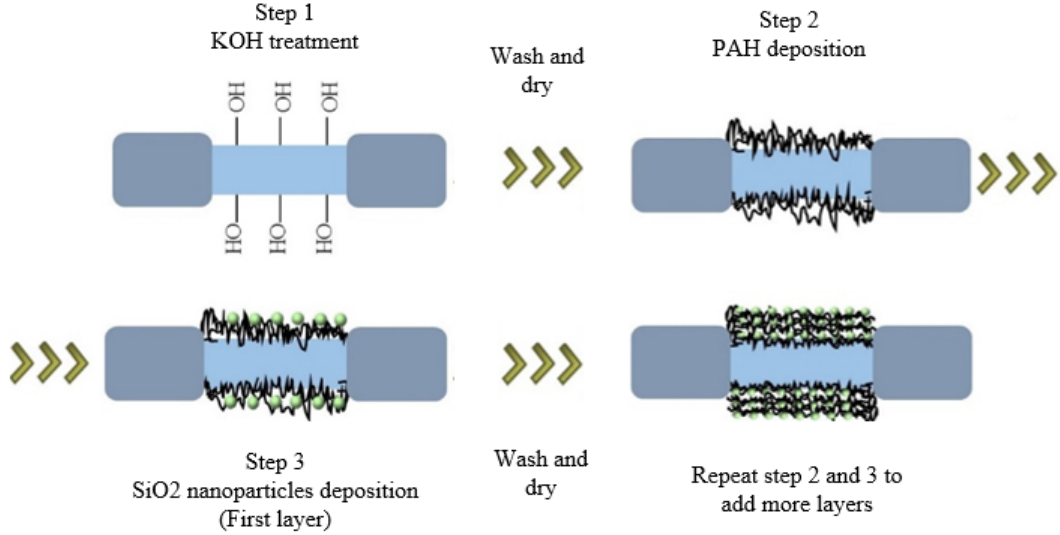


Figure 3.2: Layer-by-Layer deposition process for the fabrication of the POFHS.

3.4 In-vitro humidity measurement

The in-vitro experimental set-up for generating humidity of different levels is illustrated in Figure 3.3. Nitrogen gas is supplied to two flowmeters, F_1 and F_2 (range $0.1 - 1 \text{ L.min}^{-1}$, Cole-Parmer Instrument Co. Ltd.). F_1 supplies nitrogen gas directly to one input of a plastic three-way stopcock valve whilst F_2 is connected to a heated flask filled with water. Once evaporation of water begins, vapour is transported from the flask to the other input of the stopcock valve in order to mix flows from F_1 (direct N_2 , low humidity) and F_2 (water vapour, high humidity). The resulting combination flow provides different levels of RH. The inflow from the stopcock valve output was connected to the lid of a Petri dish via a pipe. Plastic paraffin film was used to seal the pipe with the lid and the rest of the Petri dish in order to avoid leakage.

To generate different levels of humidity the initial conditions of the flowmeters were set such that F_1 (direct N_2) and F_2 (water vapour) were fully closed (0.0 L.min^{-1}) for 2 min, i.e., the baseline humidity inside the chamber was recorded.

Measurements were then repeated with F_1 fully open (1.0 L.min^{-1}) whilst F_2 was kept fully closed (0.0 L.min^{-1}) until the signal stabilised (approximately 3.5min). Then, F_1 was reduced by 20% and F_2 was increased to 20% of full scale ($F_1 = 0.8 \text{ L.min}^{-1}$, $F_2 = 0.2 \text{ L.min}^{-1}$) until there was no change in the signal ($\sim 3.5\text{min}$). The flowmeter values were then changed in intervals of 20% until F_1 was fully closed and F_2 was fully opened.

The Petri dish acts as a measurement chamber containing the POFHS connected to the tungsten halogen light source at one end and to the spectrometer at the other end to obtain continuous measurement of the transmission spectrum as the RH was varied. In order to provide a reference standard, a commercial capacitive humidity sensor (iButton Hygrochron Temperature/Humidity Logger, DS1923, 0 to 100%RH, Maxim Integrated Ltd.) was also located inside the chamber.

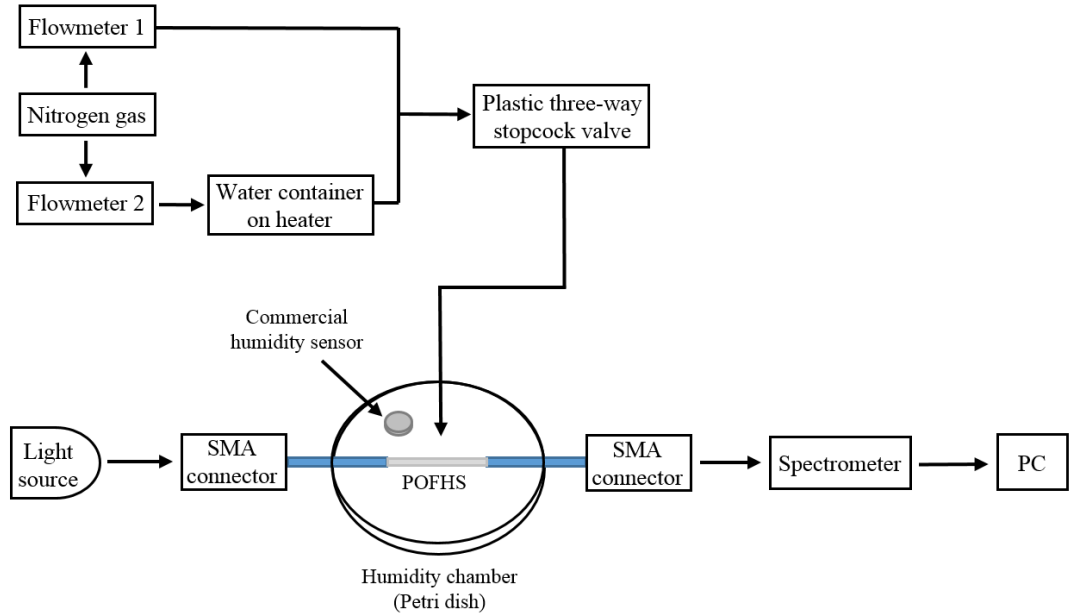


Figure 3.3: In-vitro humidity experiment with flowmeters and POFHS located inside a petri dish which acts as a humidity chamber.

3.4.1 In-vitro humidity measurement using environmental chamber

In order to perform more accurate experiments with a wider RH range and for longer periods, an environmental chamber was purchased (Bench Top, C-TH40-20/1, CVMS °Climatic Ltd., UK). The characteristics of the environmental cham-

ber are: 40L internal capacity with dimensions of 300mm $\times$ 400mm $\times$ 300mm, depth, height and width, respectively. Temperature range of -20°C to 150°C and humidity range of 30% to 98% $\pm$ 2.5% RH. The environmental chamber flows cold and hot air to change temperature and a compressor, a condenser and an evaporator are used for changing RH within the chamber. The control of temperature and RH is made by a programmable logic controller (PLC, TEMI 1500).

A series of three tests were performed using the environmental chamber to control RH and temperature conditions. In the experimental set-up, as shown in Figure 3.4, the POFHS is inserted in the centre of the environmental chamber through portholes (50mm diameter) on each side of the chamber. The tungsten halogen light source and the spectrometer are connected to each end of the POFHS to obtain measurements and compare the data obtained with the environmental chamber sensor.

The first test consisted of varying RH from 90% to 97% and vice versa with fixed temperature at 30°C to examine potential saturation of the POFHS. In the second test, temperature was changed from $\sim$ 25°C to 35°C and vice versa with RH constant at 90% to inspect cross sensitivity of RH measurements with temperature. The third test consisted of setting RH and temperature constant for a long period ($\sim$ 8hrs) at 85% and 30°C, respectively, to observe the POFHS response, repeatability and stability.

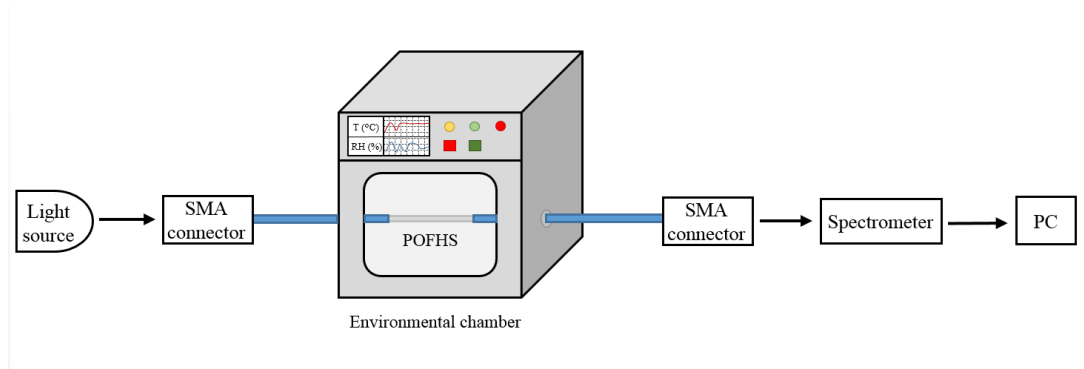


Figure 3.4: Experimental set-up for humidity and temperature test with POFHS within environmental chamber.

3.5 In-vivo humidity measurement

For the in-vivo humidity test on skin, a similar optical set-up as the above in-vitro test was deployed (Figure 3.5). The POFHS was inserted inside the measurement chamber along with the reference standard device. On this occasion the sealed lid of the chamber and the flowmeters were replaced by the palm of a human hand. The in-vivo test involved covering the chamber with the palm of the subject's hand until the output signal from the spectrometer stabilised and then removing the hand until the output signal stabilised. This process was repeated 3 times so as to ascertain repeatability of measurements. The experiment was carried out at room temperature (23°C) with measurements on 5 different volunteers (male, healthy, age 25 - 35) recorded. Before the test, all volunteers cleaned their hands with a commercial antibacterial and alcohol-free hand foam sanitiser (Ecohydra) in order to stabilise the skin to the same condition for each participant. Ethical approval was provided by the Ethics Committee, Faculty of Engineering, University of Nottingham (Appendix D).

Change in humidity levels in the previous in-vitro experiments was limited by the flowmeters and in the case here of in-vivo measurements by the release of water vapour from the skin. An additional experiment was therefore conducted to investigate the response time of the POFHS and the commercial humidity sensors by applying short rapid breaths to the measurement chamber.

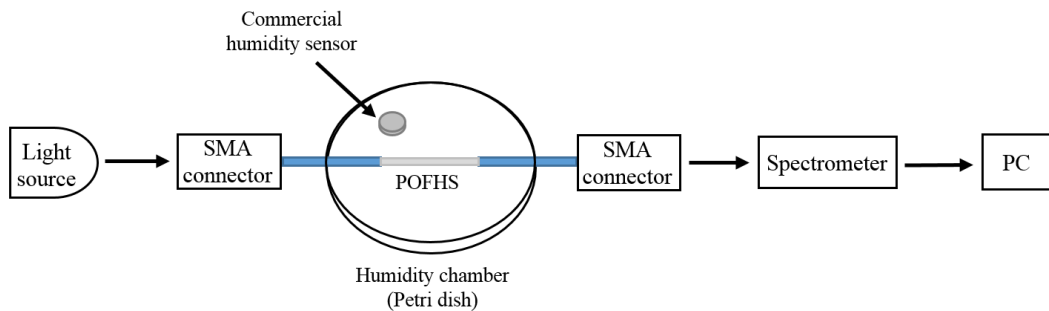


Figure 3.5: In-vivo humidity test set-up for measurements on the palm of a human hand using the POFHS.

3.6 Results

3.6.1 Sensor fabrication monitoring

The optimum core diameter for film deposition after cladding removal was $190\mu\text{m} \pm 5\mu\text{m}$ and was reached after 27 minutes immersion in acetone. At this diameter a complete removal of cladding, associated debris and a more uniform surface can be achieved, compared with $210\mu\text{m}$ core diameter as shown in the SEM images taken from the unclad section of the fibre (Figure 3.6). Further etching time produced a fragile fibre for handling and hence will not be practical for applications in wound dressings. At a core diameter of $190\mu\text{m}$ different sensing region lengths (5mm, 10mm, 20mm and 30mm) were also investigated.

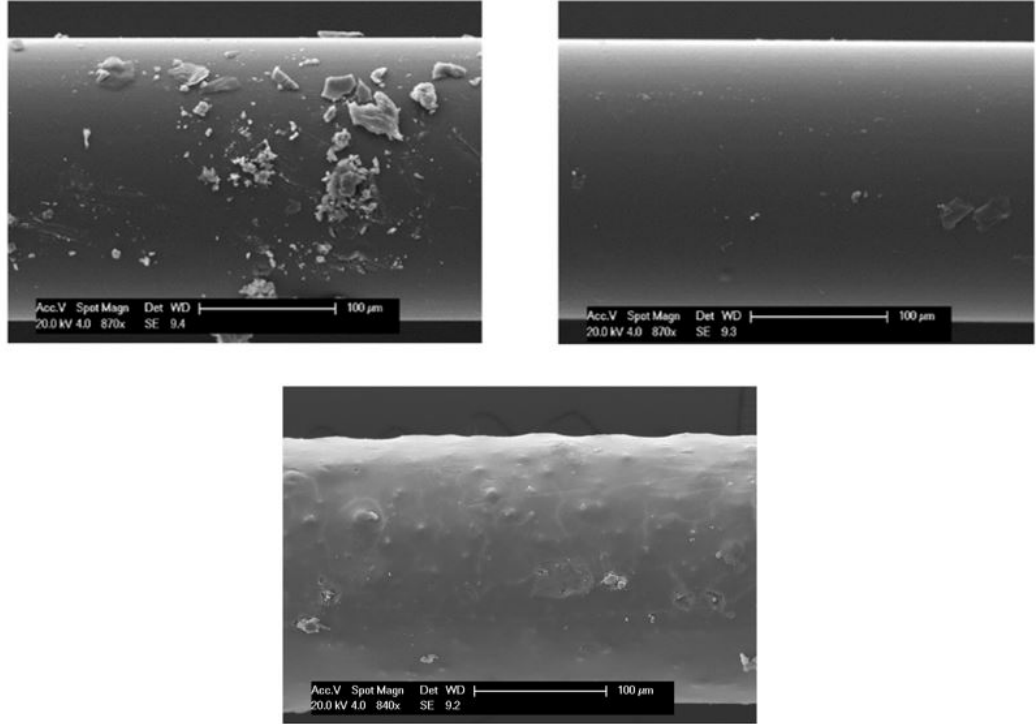


Figure 3.6: SEM image of a $210\mu\text{m}$ core diameter POF (top left) and a $190\mu\text{m}$ core diameter POF (top right) prior film deposition compared with the deposition of 7 layers of PAH/SiO₂ hydrophilic film on the exposed core (bottom, $190\mu\text{m}$ core diameter). Scale bar = $100\mu\text{m}$ in all images.

Figure 3.7 illustrates the transmittance at the peak intensity of the spectra ($\lambda = 611\text{nm}$) as a function of the unclad region length for four fibres with $190\mu\text{m}$ core diameter. It was observed that with an increased length of cladding removed, less

light intensity was transmitted to the spectrometer. This was expected since more light is able to escape from the unclad section of the fibre, which also increases the sensor interaction length with the hydrophilic film and the surrounding environment. Nonetheless, longer exposed regions produced a fragile fibre not suitable for practical applications. The standard deviation for the recorded transmittance is less than 1%, therefore error bars are not plotted on the graph.

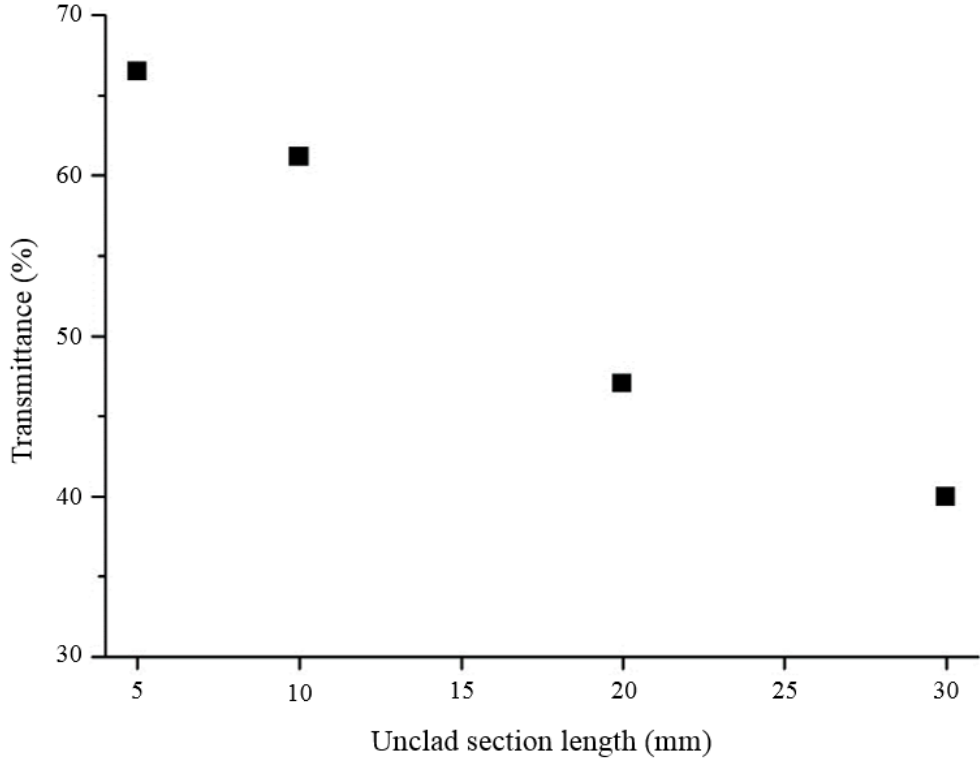


Figure 3.7: Comparison of transmittance at 611nm wavelength versus length of the unclad section of the POF after cladding removal. Core diameter = $190\mu\text{m}$.

In this project, the optimum length in terms of mechanical robustness for the unclad region of the POF was 30mm and $190\mu\text{m}$ core diameter. These values were obtained as further increment in the unclad section length and thinner fibre core produces a fragile fibre for practical applications such as the integration within textiles.

As explained in Section 1.5, the EW penetration depth can be accessed by removing the fibre cladding to interact with a sensitive element (in this case, PAH/SiO₂ layers) and the environment (in this case, the humidity around the sensing region)

[174, 192, 193]. Figure 3.8 illustrates the increment in light intensity (given by the amount of photons detected by the spectrometer and expressed as a digital number, DN) versus wavelength as more layers are added to the unclad section of the fibre for the whole spectra whereas Figure 3.9 shows the transmittance at the peak intensity wavelength ($\lambda = 611\text{nm}$) as the number of layers increases. The transmittance increases with the number of layers due to the interaction with the EW penetration depth at the sensitive region of the fibre, which depends on the wavelength of the light launched into the fibre core, the refractive index of the hydrophilic film and the angle of incidence.

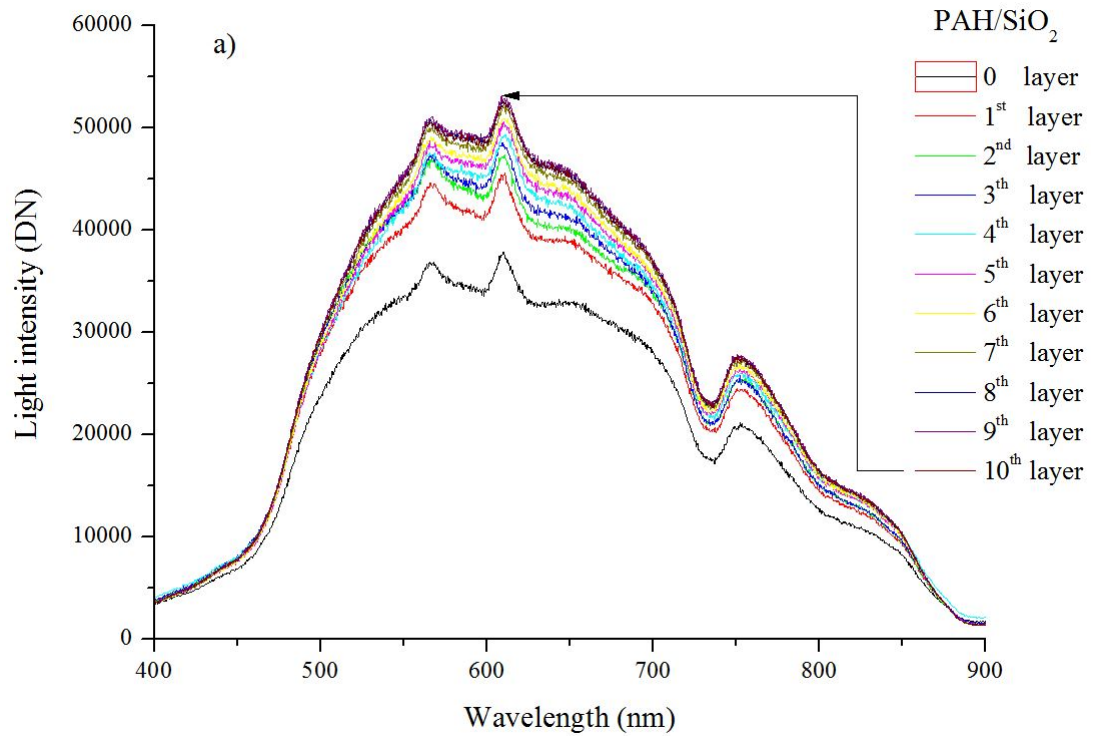


Figure 3.8: POFHS light spectra along film deposition which illustrates that as more layers are deposited light intensity increases. Unclad region length = 30mm, fibre core diameter = 190 μm .

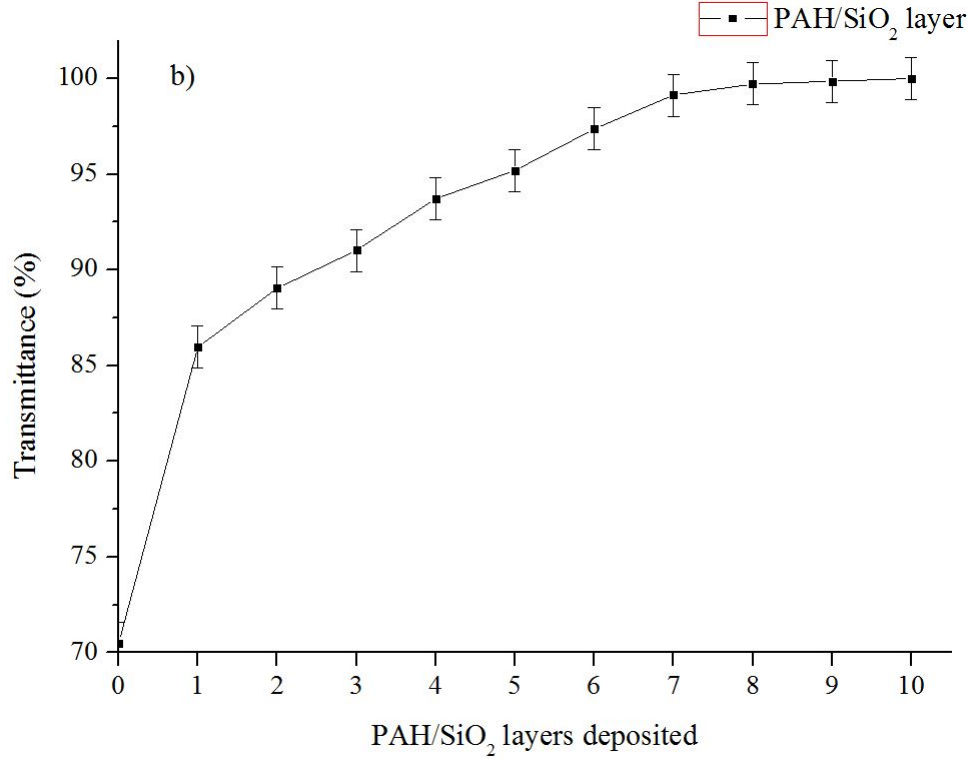


Figure 3.9: POFHS transmittance at peak intensity of the spectra ($\lambda = 611\text{nm}$) versus number of layers deposited. Unclad region length = 30mm, fibre core diameter = $190\mu\text{m}$.

After depositing the 7th layer, it can be seen that only a small change in intensity occurs. This can be explained with reference to the relationship between the EW penetration depth and the film thickness. The optimum film thickness needs to be lower than or equal to the EW penetration depth as sensitivity decreases due to the lack of interaction between EW and the surrounding environment [78].

In this case, a single layer of the hydrophilic film composed of PAH/SiO₂ layers has a refractive index of 1.2000 ± 0.0006 [194]. The critical angle, θ_c (Equation 1.2), with respect to the hydrophilic film, i.e., at the sensitive region is $\sim 54^\circ$. Moreover, as the angle of incidence, θ_i , approaches θ_c , the EW penetration depth increases. However, the EW penetration depth is considered as the value where the depth decreases to the $1/e$ value, as explained in Section 1.5 and illustrated in Figure 3.10.

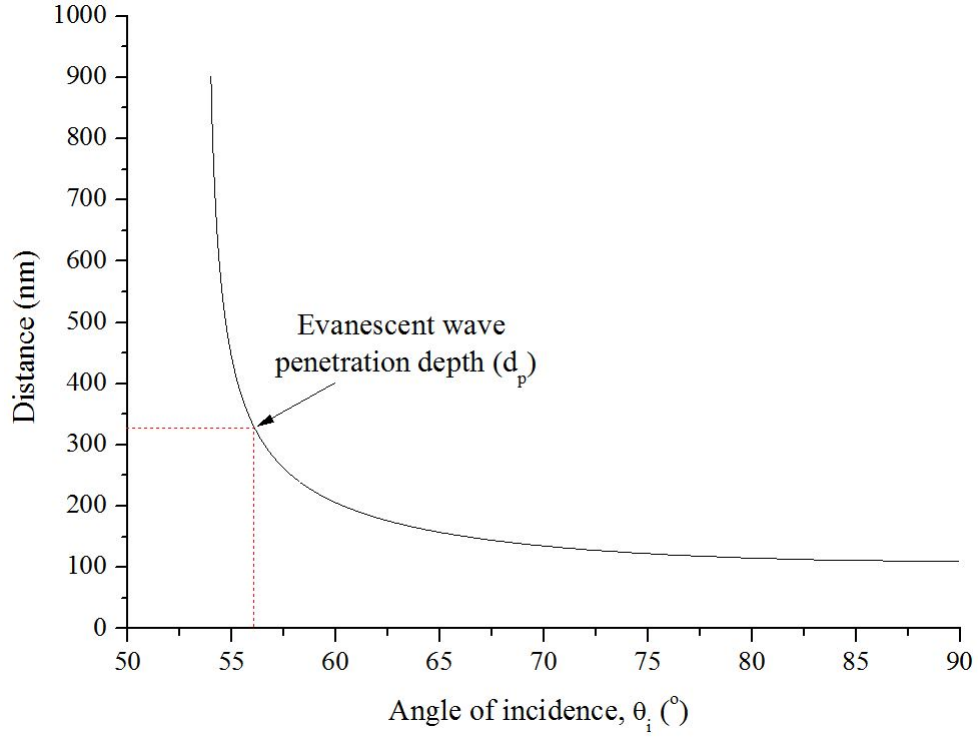


Figure 3.10: Evanescent wave penetration depth in the POFHS.

The EW penetration depth (calculated with Equation 1.4) at the sensitive region of the fibre for the intensity peak wavelength ($\lambda = 611\text{nm}$) and $\theta_i \approx \theta_c$ is $\sim 343\text{nm}$. Since a single PAH/SiO₂ layer is approximately $46 \pm 3\text{nm}$ thick [194], after 7 layers are deposited (Figure 3.6, bottom) the film thickness is close to the EW penetration depth producing higher interaction between the EW and the hydrophilic film, hence the sensitivity is increased.

3.6.2 In-vitro humidity measurement based on flowmeter set-up

The intensity at the 611nm wavelength peak is illustrated in Figure 3.11 for a fibre with $190\mu\text{m}$ core diameter and 7 PAH/SiO₂ layers deposited on a 30mm sensitive region (red trace) compared to the capacitive commercial humidity sensor (blue trace). As can be seen, the POFHS can clearly detect humidity changes and also has a faster response time compared with the capacitive humidity sensor as the RH was changed. The sensor settling time is defined as the time at which the light intensity stabilises within 2% of the maximum value recorded for humidity level. The average settling time for the POFHS was 23s whereas for the commercial sensor the average settling time was 45s. It should be noted that this is not representative of the actual response time of the POFHS as the change in

the humidity in the chamber is gradual.

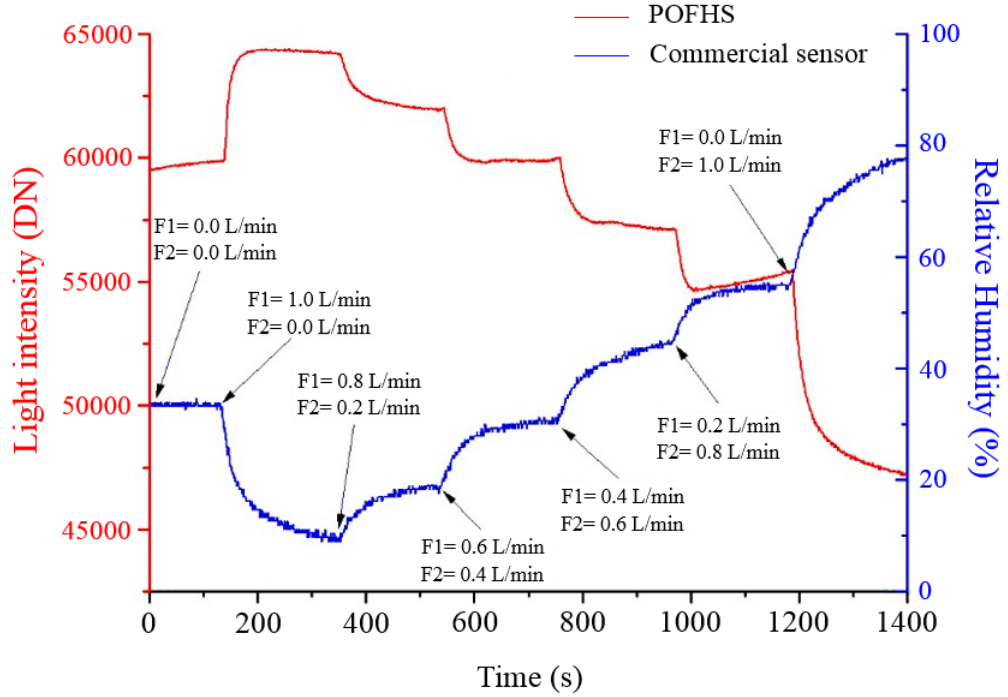


Figure 3.11: In-vitro humidity measurement with flowmeters F_1 and F_2 gradually adjusted in steps of 20% to vary humidity in the chamber. All results were monitored at 611nm wavelength for the POFHS with 7 PAH/SiO₂ layers deposited (sensor length = 30mm, fibre core diameter = 190 μ m, red trace). Humidity measurements recorded with a commercial capacitive humidity sensor (iButton Hygrochron Temperature/Humidity Logger, DS1923, 0 to 100%RH, Maxim Integrated Ltd., blue trace).

Figure 3.12 shows the calibration curves for in-vitro humidity measurements with a POFHS (190 μ m core diameter and 30mm sensitive region length) coated with 5, 7 and 10 PAH/SiO₂ layers. Measurements were taken at 611nm wavelength. Error bars show the comparison of a set of multiple POFHSs coated with 5, 7 and 10 PAH/SiO₂ layers to observe repeatability. It can be observed that the POFHS sensitivity increases as the number of layers increases. After 7 PAH/SiO₂ layers are deposited, the POFHS demonstrated a sensitivity (-3.87×10^{-3} in transmittance percentage per RH percentage for the range of $\sim 10\%$ to $\sim 75\%$ RH. However, after 10 layers deposited, the sensitivity decreased due to the lack of interaction with the EW. The thickness of 7 PAH/SiO₂ layers is the closest to the EW penetration depth and provides optimal performance, since higher interaction of EW and the hydrophilic film can be achieved.

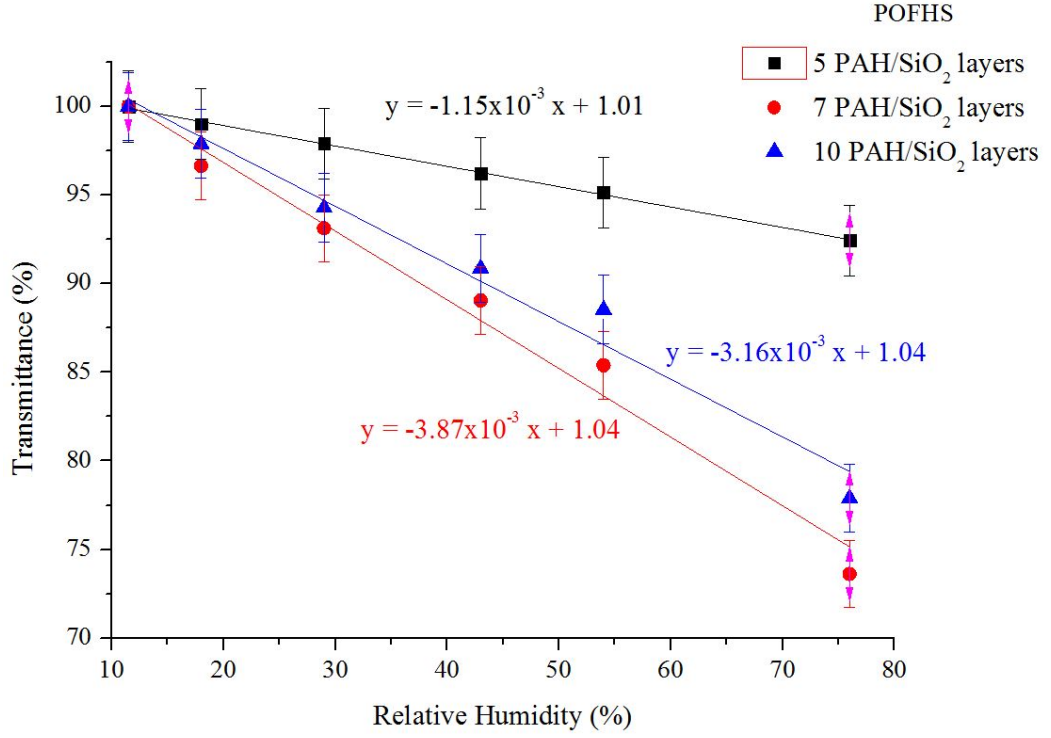


Figure 3.12: In-vitro calibration curves of a set of POFHSs coated with 5, 7 and 10 PAH/SiO₂ layers. Measurements were taken at 611nm wavelength, 190 μ m core diameter and 30mm sensitive region length for all sensors. RH range from $\sim$ 10% to $\sim$ 75%. Error bars show the comparison of a set of multiple POFHSs coated with 5, 7 and 10 PAH/SiO₂ layers.

3.6.3 In-vitro humidity measurement based on environmental chamber

Figure 3.13a shows the results for the first test performed with the environmental chamber set-up where RH was changed from 90% to 97% and vice versa every 30 minutes. The temperature was set constant at 30°C (Figure 3.13b) throughout. It can be noted that the POFHS response (red trace) is following the trend of the humidity change measured using the environmental chamber sensor (blue trace). Repeatability can be observed in the measurements recorded at 611nm wavelength for the POFHS with 7 PAH/SiO₂ layers, Figure 3.13a. The linearity observed shows a sensitivity of -9.61×10^{-3} in transmittance percentage per RH percentage in the range of 90% to 97% RH, Figure 3.14.

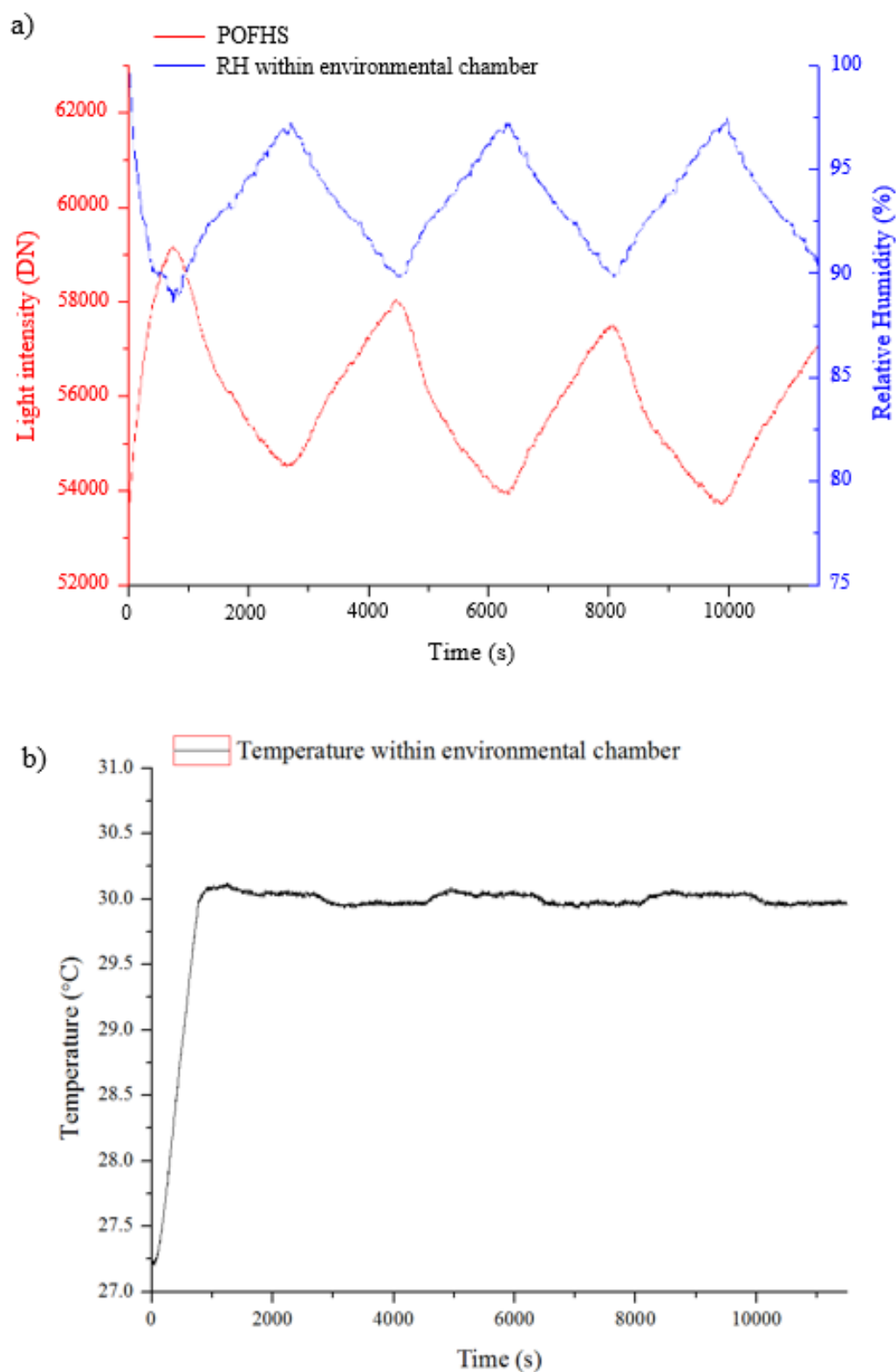


Figure 3.13: First test with POFHS with 7 PAH/SiO₂ layers within environmental chamber set-up. (a) POFHS (red trace) and environmental chamber sensor (blue trace) response to humidity in the range of 90% to 97% RH. (b) Temperature recorded during the test, set at 30°C

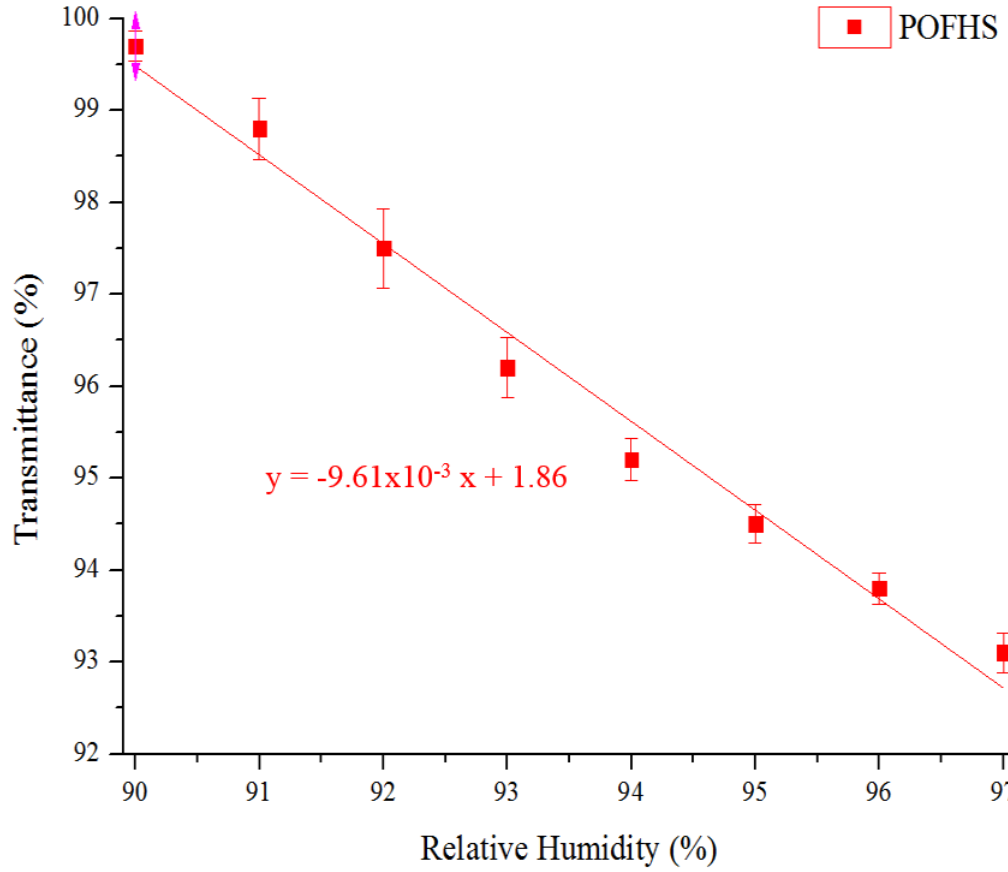


Figure 3.14: Calibration curve of POFHS coated with 7 PAH/SiO₂ layers. Measurements were taken at 611nm wavelength, 190 μ m core diameter and 30mm sensitive region length. RH range from 90% to 97%.

The second test consists of cycling the temperature from $\sim 25^{\circ}\text{C}$ to 35°C while trying to maintain RH at 90% using the environmental chamber. Since temperature and RH are related, it can be seen that RH fluctuates (Figure 3.15a) as temperature was changed from $\sim 25^{\circ}\text{C}$ to 35°C (Figure 3.15b) and backwards. Nevertheless, the POFHS behaviour is proportional to that recorded by the environmental chamber sensor (red trace, Figure 3.15a) which indicates that the POFHS is sensitive to the RH rather than to the temperature. It should be also noted that RH sensor from the environmental chamber saturates at 100% (blue trace, Figure 3.15a) and cuts the top off the readings, while the POFHS continuously measures the change in RH. The behaviour of the environmental chamber RH sensor is most likely due to the in-accuracy of the RH sensor which is quoted as $\pm 2.5\%$ and measurement range of up to 98%.

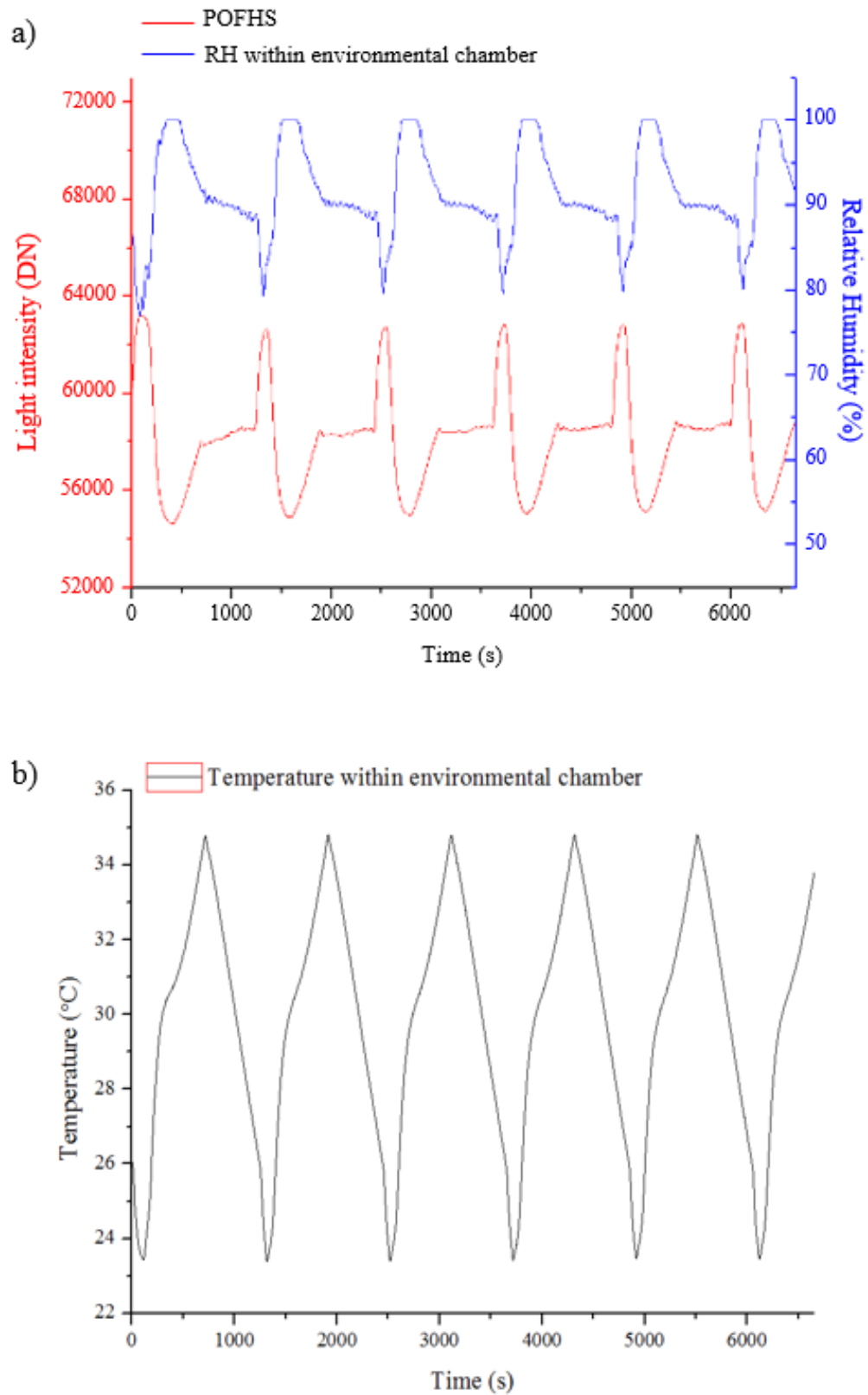


Figure 3.15: Second test with POFHS with 7 PAH/SiO₂ layers within environmental chamber set-up. (a) POFHS (red trace) and environmental chamber sensor (blue trace) response of RH fluctuation as temperature changes. (b) Temperature change from 23.5°C to 35°C and vice versa.

In the third test, the POFHS response was measured for a long period with constant RH and temperature at 85% and 30°C, respectively. As can be seen in Figure 3.16a, the POFHS response is stable compared with the environmental chamber sensor. Using the calibration curve (Figure 3.14), the POFHS signal can be expressed in terms of RH, Figure 3.16b. It can be noticed that the POFHS response is reliable for long term measurements. This opens up the possibility for it to be used in many other applications such as the continuous monitoring of wound healing for example.

In addition, in order to further understand the behaviour of the POF, an optical fibre with cladding removed (30mm unclad section length, 190 μ m core diameter) without film coating was inserted within the set-up during the long period test. As can be seen in Figure 3.16a, the response of the unmodified fibre (black trace) is not stable at fixed values of RH compared with the POFHS signal. This phenomenon most plausibly is owing to the swelling of the POF. On the other hand, the POFHS (i.e., modified with the sensitive film of 7 PAH/SiO₂ layers) has a stable response, most likely owing to the protection role that the 7 PAH/SiO₂ layers play and adsorb water molecules preventing them from absorption inside the POF. Moreover, using the calibration curve from Figure 3.14 the POFHS measurements can be expressed in RH percentage in order to compare it with the values recorded with the environmental chamber, as shown in Figure 3.16b.

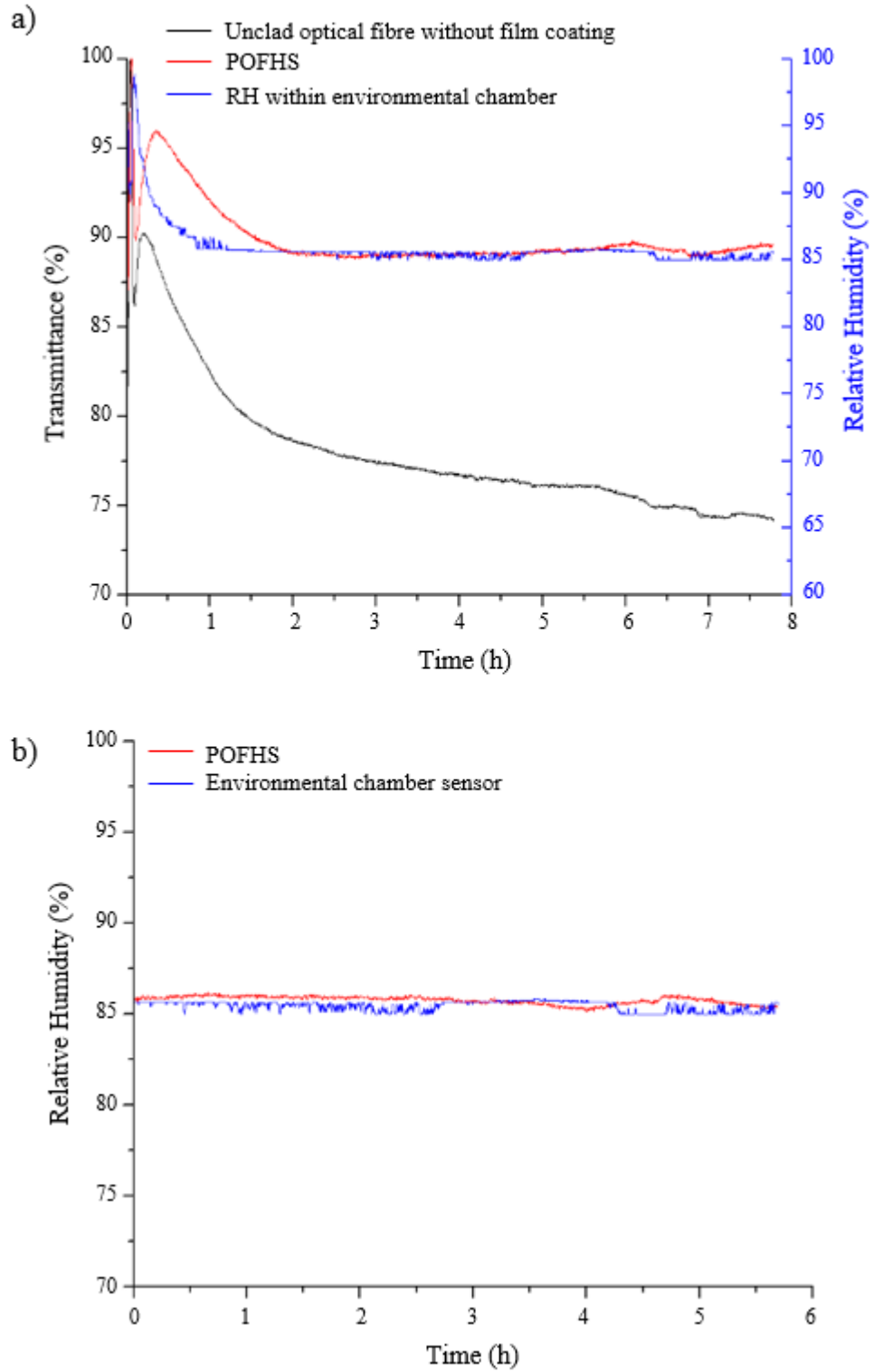


Figure 3.16: Third test with environmental chamber set-up. (a) POFHS (red trace), environmental chamber sensor (blue trace) and optical fibre without film and core exposed (black trace) response to continuous RH measurements. Temperature and RH constant at 30°C and 85%, respectively for approximately 8hrs. (b) POFHS readings (red trace) in terms of RH compared with environmental chamber sensor (blue trace).

3.6.4 In-vivo humidity measurements

The purpose of the in-vivo humidity test was to monitor the RH present on the skin microenvironment at the palm of the hand to mimic the wound environment. As described previously, the study consisted of placing the palm of the hand on the petri dish measurement chamber as shown in Figure 3.5 and monitoring transmittance in order to observe the RH changes within the chamber. The hand was removed from the top of the chamber after the signal stabilised.

Figure 3.17 shows the results for the in-vivo humidity measurements on skin for one of the participants at 611nm wavelength since similar results were obtained with all the volunteers. Using the calibration curve (Figure 3.12), the signal obtained from the POFHS can be observed in terms of RH in order to measure the response time compared with the commercial sensor. The variation of RH recorded for each participant was from $50 \pm 5\%$ to $90 \pm 5\%$. When removing the hand from the chamber, a rapid drop in RH occurs due to the difference between the RH inside the measurement chamber and the environment. This sudden RH change is observed in both the POFHS and the commercial humidity sensor signals. The hand was placed again on the chamber after the signal stabilised again. This operation was repeated 3 times in order to investigate repeatability of the measurements for each volunteer. The settling time, which is the time for the signal to reach 90% of saturation value was $100 \pm 3s$ and $135 \pm 3s$, for the POFHS and the commercial sensor, respectively. As expected, the same behaviour as for the in-vitro humidity measurements was observed, i.e. an increase in RH represents a decrease in light intensity. Again, these response times are limited by the rate of humidity increase in the chamber and not the response time of the sensors.

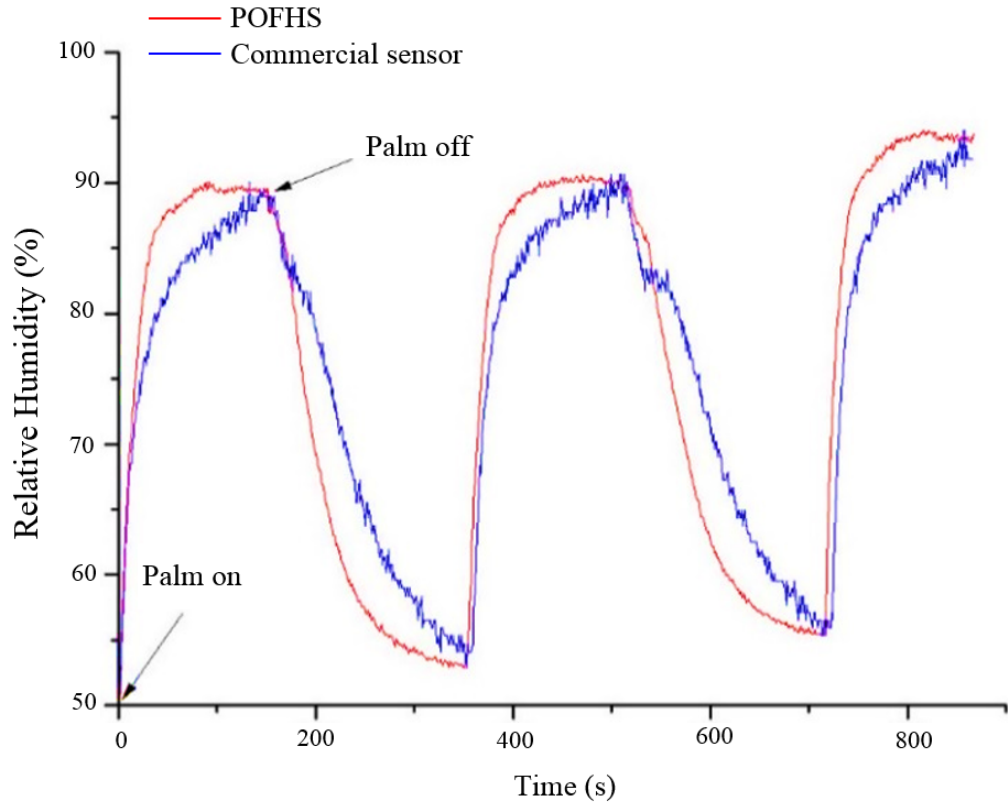


Figure 3.17: In-vivo humidity measurements on the palm of the hand recorded with the POFHS (red trace) and the commercial humidity sensor (blue trace).

In order to further investigate the POFHS response time, a more rapid change in humidity is provided using a sharp breath on the sensor. Figure 3.18 displays RH measured at 611nm wavelength for the POFHS (red trace) along with the commercial humidity sensor response (blue trace) in RH. The response time is calculated as the time from 10% to 90% of the final recorded value. The POFHS response time recorded was 1.5s, whereas the value observed with the commercial sensor was 3.6s.

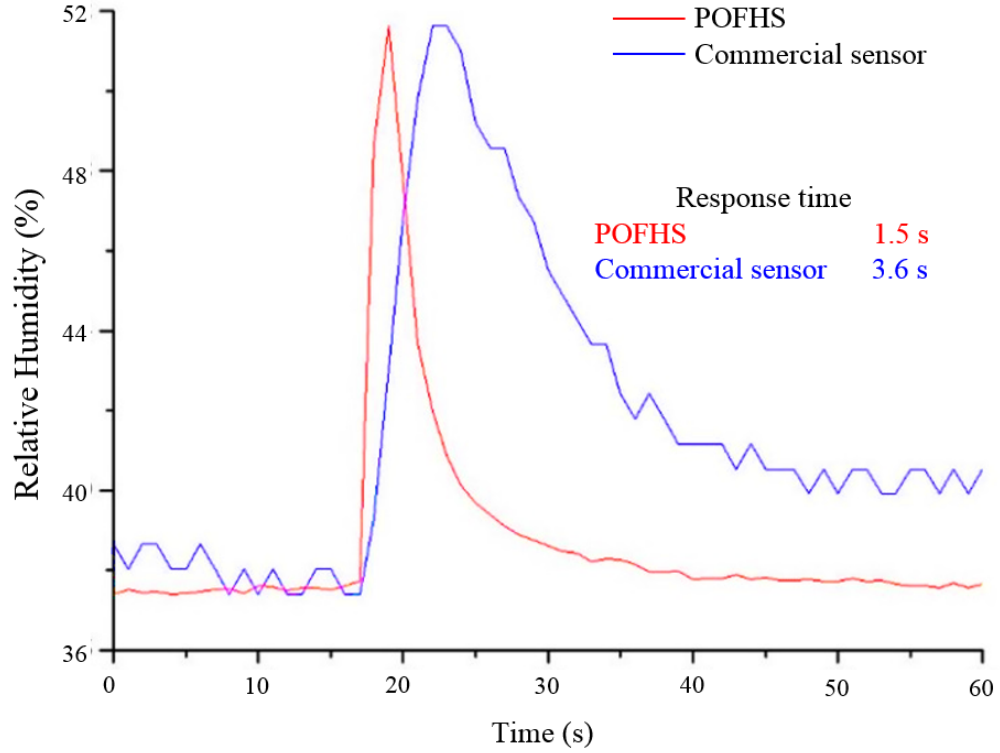


Figure 3.18: Response time of POFHS and commercial humidity sensor in response to a single breath on both sensors simultaneously.

3.7 POFHS within dressing

As a first step for wound monitoring development, the POFHS has been embedded in a dressing (sterile, N-A knitted viscose primary dressing, Systagenix Wound Management Ltd., UK) with dimensions 9.5cm length and 9.5cm width and it was covered by a clinical gauze used as secondary dressing (non-woven swab clinic gauze, Clinisupplies Ltd., UK) with dimensions 5cm length and 5cm width in order to observe its feasibility for humidity measurements, as shown in Figure 3.19a. In order to observe the POFHS response embedded on the dressing, the in-vivo humidity experiment was performed for a single volunteer (male, healthy, age 26). Ethical approval was provided by the Ethics Committee, Faculty of Engineering, University of Nottingham (Appendix D).

Figure 3.19b shows the response of the POFHS to the RH generated by the palm of the hand. As can be seen on the graph, the behaviour of the POFHS is similar to the previous in-vivo test in Section 3.4. Nonetheless, since the POFHS is

embedded on the dressing and it is covered by a clinical gauze, a longer settling time is observed. It should be noted that the response is highly dependent on the properties of the textile and further work investigating responses of different wound dressings will form part of future work.

The settling time and the recovery time obtained were $\sim 7.7\text{min}$ and $\sim 9.7\text{min}$, respectively. The RH change observed was between $30\% \pm 2\%$ and $95\% \pm 2\%$. These are encouraging results in order to develop a dressing that can remotely monitor humidity in the skin microenvironment and that can be helpful to provide better prognosis of wound healing.

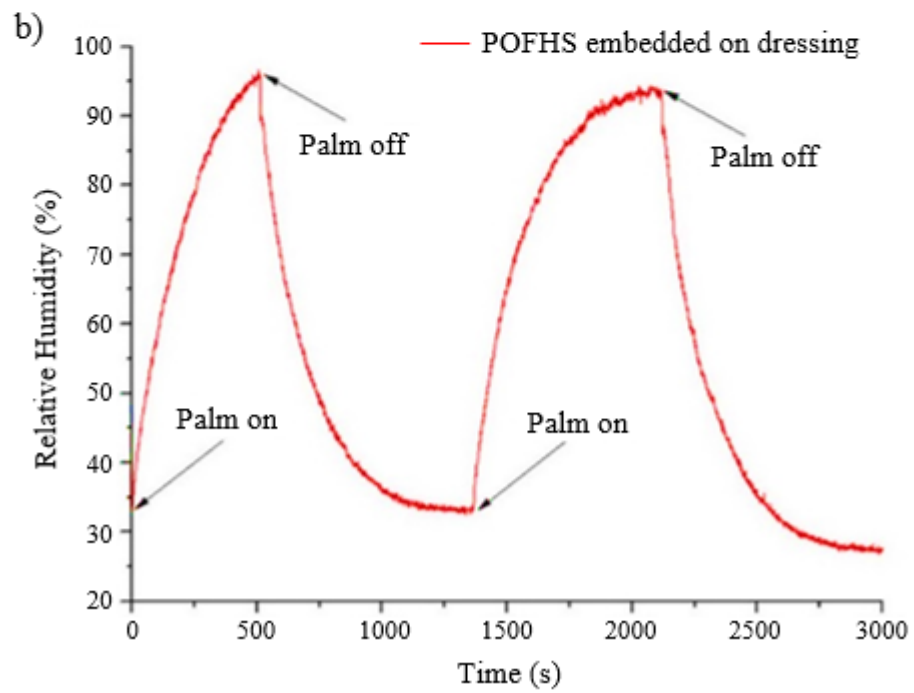
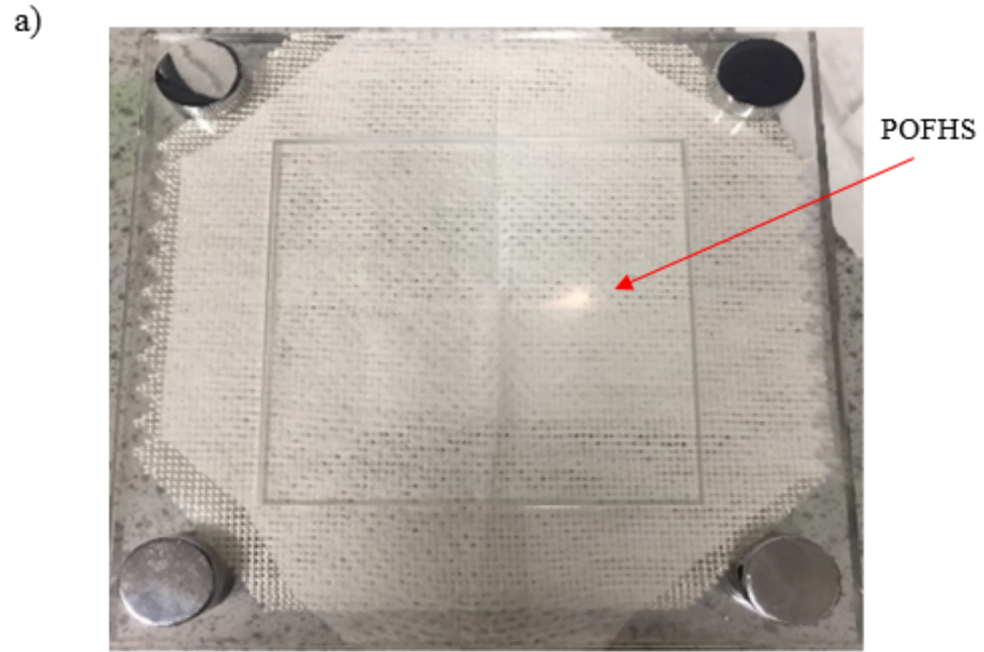


Figure 3.19: (a) POFHS embedded in a dressing and covered by a clinical gauze as a secondary dressing for humidity measurements. The unclad visible part of the sensor is 30mm length. (b) In-vivo humidity measurements on the palm of the hand recorded with the POFHS embedded on a dressing and covered with a clinical gauze as secondary dressing.

3.8 Summary and comments

In this chapter, it was demonstrated that a POF coated with PAH/SiO₂ layers on the exposed core can be used as a humidity sensor. A higher RH sensitivity can be obtained by optimising the film thickness depositing 7 PAH/SiO₂ layers which is close to but lower than the EW penetration depth. The sensitivity demonstrated for 7 layers deposited was -3.87×10^{-3} and -9.61×10^{-3} in transmittance percentage per RH percentage for the range of $\sim 10\%$ to $\sim 75\%$ RH and 90% - 97% RH, respectively.

The deposition of SiO₂ nanoparticles as a sensitive element has provided pilot data to illustrate its efficiency in the detection of humidity. The RH measurements in the in-vivo tests suggests that the POFHS developed can be used as a humidity sensor of the human skin. The POFHS response time is in the order of 1.5s compared to the commercial humidity sensor of 3.6s, for breath monitoring (rapid RH changes). In addition, for measurements on skin, the POFHS average settling time observed was 1.6min, faster than settling time recorded by the commercial sensor (~ 2.6 min). Further, the POFHS feasibility to be integrated within a dressing was tested by embedding the POFHS into a textile. The results obtained suggests that a POFHS within a dressing can be developed in order to monitor moisture in wounds.

The development of POFHS is a novel technology that provides a faster response, compared with a commercial humidity sensor. The POFHS advantages are flexibility, ease of incorporation into dressings and immunity to electromagnetic fields. This new and reliable unobtrusive approach for humidity sensing is potentially extremely helpful for providing improved monitoring of wound status. If successful it will be of increased benefit for patients and offers the potential to allow a better understanding about the process of wound healing itself.

Chapter 4

Optical Fibre pH Sensor

"If you would be a real seeker after truth, it is necessary that at least once in your life you doubt, as far as possible, all things."

- Rene Descartes -

4.1 Introduction

The measurement of pH is of crucial importance for application fields such as industry, medicine and food processing [195, 196]. Currently, there exists different techniques to monitor pH, however some instruments lack accuracy, require frequent re-calibration or are not suited to be used in-situ due to their size or fabrication materials [131, 177]. For these reasons, the development of OFS for pH measurements has been increasing throughout the years [129].

In Section 2.3 some of the OFS developed for pH sensing are described. Most of the sensors share the same principle of operation, i.e., the use of a sensitive film based on an indicator such as a dye compound to monitor pH according to the light spectra changes observed [197]. Porphyrins, which consists of a heterocyclic macrocycle composed by a pyrrole ring, are commonly used as a sensitive element due to its absorption spectrum which is characterized by one or two absorption peaks at around 400nm. This, is known as the Soret band, and up to four less intense absorption peaks (in the case of metalloporphyrins and free-base porphyrins, respectively) at the wavelength region from 450nm to 700nm, which are considered as Q bands [198]. These absorption bands can be broadened, split or red/blue shifted under certain conditions, for example, during protonation [199].

Moreover, the OFS with U-shape configuration has an increased EW which can be useful to obtain higher sensitivity which can lead to pH measurements with higher resolution. In addition, since this configuration can be easily coated by dip-coating method, the sol-gel material has been found as the preferred sensitive coating due to its ease of fabrication which can be made at low temperatures producing a matrix that can entrap sensitive molecules for interaction with the environment [137, 181, 200].

In this chapter, the fabrication of a fibre optic pH sensor with a U-shape configuration is described. Dip-coating technique was used to coat the sensitive region of the fibre with a sol-gel solution. Tetraethyl orthosilicate (TEOS) was used as precursor whereas tetrakis(4-sulfonatophenyl)-porphyrin (TSPP) was selected as a pH indicator. EW absorption measurements were taken over pH modification.

The purpose of this sensor is to detect pH in a short range close to neutral pH in order to provide an approach to help clinicians in the analysis of wound healing (for example, wound exudate pH) [34] or during foetal blood sampling (FBS) to help to obtain more information to make a decision for foetal delivery [53].

4.2 Materials and instrumentation

Multi-mode optical fibre (0.39 NA, Thorlabs Ltd.) with $200\mu\text{m}$ silica core diameter and $225\mu\text{m}$ diameter technology enhanced hard clad silica (TECS) was deployed. The core and cladding refractive indices are 1.45 and 1.39, respectively. A halogen light source (Ocean Optics HL - 2000, wavelength range $\lambda = 360 - 2400\text{nm}$) and a spectrometer (Ocean Optics USB 2000+, detection range $\lambda = 200 - 1100\text{nm}$) were used to obtain absorption measurements. SMA connectors were used to connect each end of the optical fibre to the light source and the spectrometer. A butane gas blow torch (2200 VersaFlame, Dremel, Netherlands) was used for the U-shape fabrication.

The sol-gel was prepared using a magnetic stirrer (RTC basic, 50 - 1500rpm speed, IKA labortechnik) and a magnetic stir bar of 20mm. The film deposition was accomplished by dip-coating using a dip coater based on a PC-controlled stepper-motor controller (C-663 mercury step controller) connected to a high-resolution translation stage (compact linear stage with crossed roller bearings, $0.1\mu\text{m}$ minimum incremental motion, 80nm resolution, 6mm.s^{-1} max speed, 25mm travel range), both obtained from PI Physik Instrumente Ltd., UK. A commercial handheld pH meter with a glass electrode (PHH-37, 0 - 14 pH range, 0.01 resolution, ± 0.03 accuracy, 1s sampling rate, RS232 serial communication, Omega Engineering Ltd., UK) was used to compare with the OFS pH measurements.

4.3 Sensor fabrication

The optical fibre pH sensor developed follows the U-shape configuration in order to further increase the EW penetration depth and hence the interaction of the sensitive region with the environment, as explained in Section 1.5. Additional to

this, the deposition of the film by dip-coating technique is easily achieved with the U-shape optical fibre. A butane gas torch was used to burn off the fibre cladding and produce the U-shape configuration.

To create the U-shape, the fibre was fixed on a holder as illustrated in Figure 4.1. The cladding from the middle section of the fibre was removed by exposing it to a sharp butane flame until the fibre bent into a U-shape. This set-up provides a controlled fibre bending to obtain consistent bending radius compared with manually bending the fibre [78].

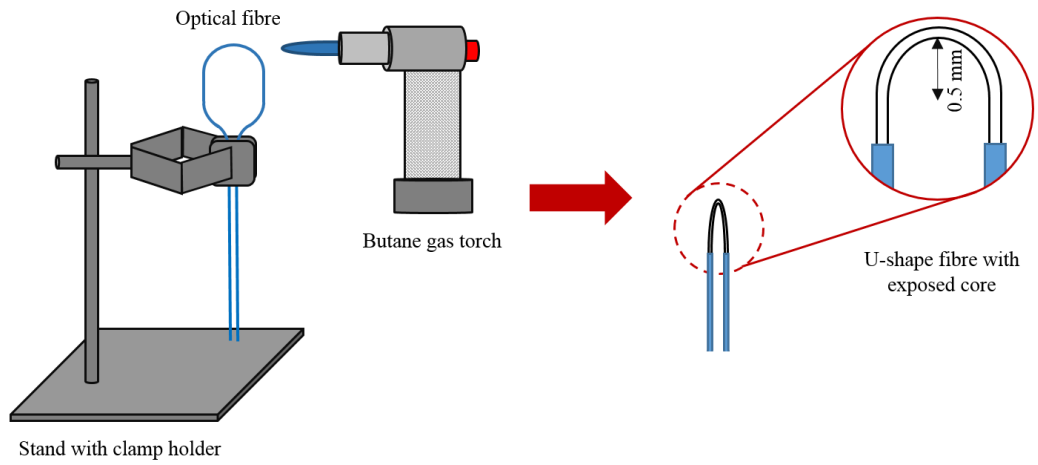


Figure 4.1: Fibre optic U-shape bending.

As explained in Section 1.5, there exists a proportional relationship between the bending radius and the sensitivity due to the light rays travelling at different angles at the outer (Equations 1.5 and 1.6) and inner surfaces (Equation 1.7) of the U-shape which increases the EW, i.e., the smaller the bending radius the higher the sensitivity [201, 202, 203]. Taking into consideration this principle, the smallest bending radius obtained with this set-up was 0.5mm and the typical length of blow torch time was 2s.

To further observe the sensitivity comparison among different bending radii, a set of 9 fibres with a range of 1.5 - 0.5mm bending radius were produced. The set of fibres were immersed into ethanol (EtOH) solutions in water. The EtOH concentration was increased from 20% - 60%. The refractive index in the solution increases as the concentration of EtOH is raised, hence attenuation of light can

be compared among the set of fibres to select the fibre with the higher sensitivity according to the bending radius [81, 204, 205].

Once the fibre U-shape is produced, the sensitive film is prepared. In Section 1.5.2 it was explained the elements required for the sol-gel formation. In this work, to prepare a pH sensitive film, TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Mw} = 208.33 \text{ g.mol}^{-1}$, 0.933 g.mL^{-1} density, 1.38 refractive index) was used as precursor to obtain a coating with lower refractive index than that from the fibre core, hence, achieving TIR. Since TEOS is immiscible in water, EtOH was used as solvent used for hydrolysis. On the other hand, TSPP ($\text{Mw} = 934.99 \text{ g.mol}^{-1}$, 5mM in water), a dye compound purchased from Tokyo Kasei Japan, was selected as the pH indicator.

TSPP is a water-soluble porphyrin that has been previously studied and used in applications namely: detection of volatile organic compounds (VOCs); chemical level detection (such as ammonia); and in medical applications (for example as a photosensitizer for tumour location in photodynamic therapy (PDT) or as a sensor for DNA concentration) [206, 207, 208, 209] due to its high fluorescence and its non-toxicity for in-vivo settings [210, 211]. Figure 4.2 depicts the TSPP molecular structure [212, 213]:

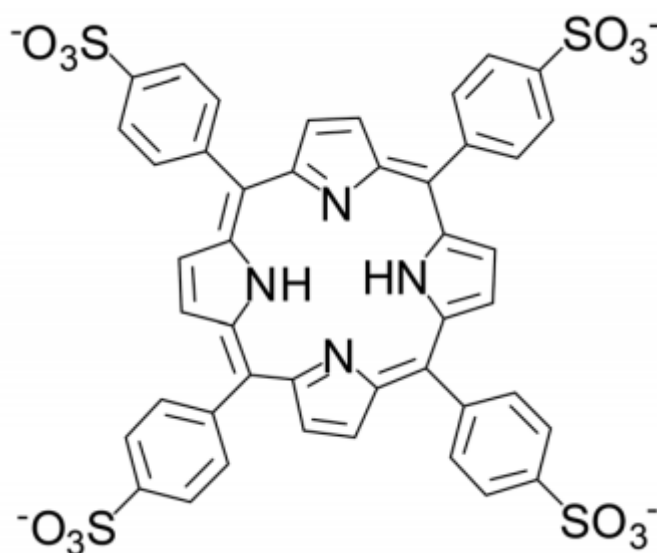


Figure 4.2: Tetrakis(4-sulfonatophenyl)-porphyrin (TSPP) molecular structure in free-base form (deprotonated).

To prepare the pH sensitive film, 2ml of TEOS (2.2M), 1ml of EtOH (4.2M) and 1ml of TSPP (5mM) were mixed. A magnetic stirrer was used to mix the chemicals for 1hr at 600rpm speed. After the mixing, the solution was kept for aging for 24hrs prior the fiber coating process.

As explained in Section 1.5.2, the sol-gel film can be coated onto the optical fibre sensitive region by spin-coating, dip-coating or spray-coating technique. In this work, dip-coating was selected to coat the exposed core of the U-shape fibre following the set-up shown in Figure 4.3. For this method, the film thickness is determined by the withdrawal speed. Slower withdrawal speed produces a thin film with an increased concentration since a constant deposition and drying of the film is achieved [139, 214, 215].

Additional to this, in Chapter 3 it was studied the relationship between the EW penetration depth and the film thickness, which is required to be equal to or lower than the EW penetration depth in order to guarantee the interaction of light with the surrounding environment in the sensing region [78]. Studies have demonstrated that the withdrawal speed of $\leq 1\text{mm.s}^{-1}$ provides optimum film thickness for the dip-coating method [78, 185, 216]. To prove this concept two different withdrawal speed (1mm.s^{-1} and 6mm.s^{-1}) were selected.

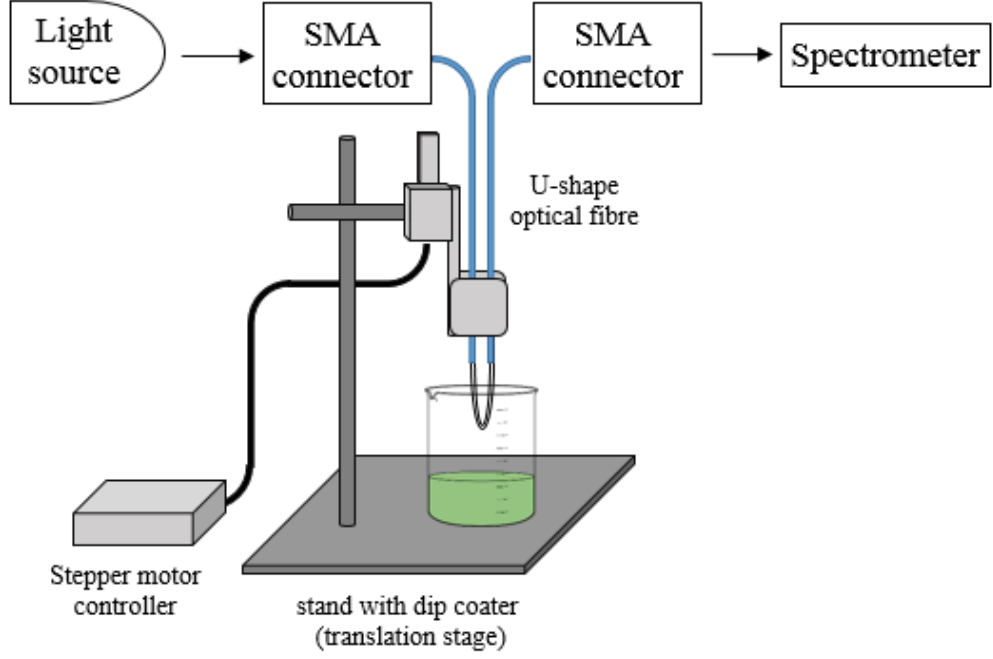


Figure 4.3: Set-up for pH sensitive film deposition onto U-shape optical fibre.

4.4 pH test set-up

After the sensor fabrication, the optical fibre pH sensor performance was tested. Measurement of pH was taken with the set-up represented in Figure 4.4. This set-up consisted of a stand with a clamp holder to fix the OFS. The sensor was immersed in the centre of a glass beaker filled with pure water (150ml) which was supported by a magnetic stirrer. A commercial pH meter electrode was also immersed into the beaker to compare the measurements with the optical fibre pH sensor. To modify the pH, solutions of HCl and NaOH in water (both at 1M concentration) were prepared. A magnetic stirrer bar rotating at 500rpm was placed at the bottom of the beaker to obtain a uniform pH across the solution while adding HCl or NaOH to move the pH value to an acid or a base region, respectively. The experiment was carried out at a constant temperature, recorded also by the commercial pH meter (23 °C). Absorbance measurements were obtained by following Equation 4.1:

$$A(\lambda) = \log_{10} \left(\frac{T_0(\lambda)}{T(\lambda)} \right) \quad (4.1)$$

Where λ is the measured wavelength, $T_0(\lambda)$ and $T(\lambda)$ are the initial and final transmittance values at the selected wavelength.

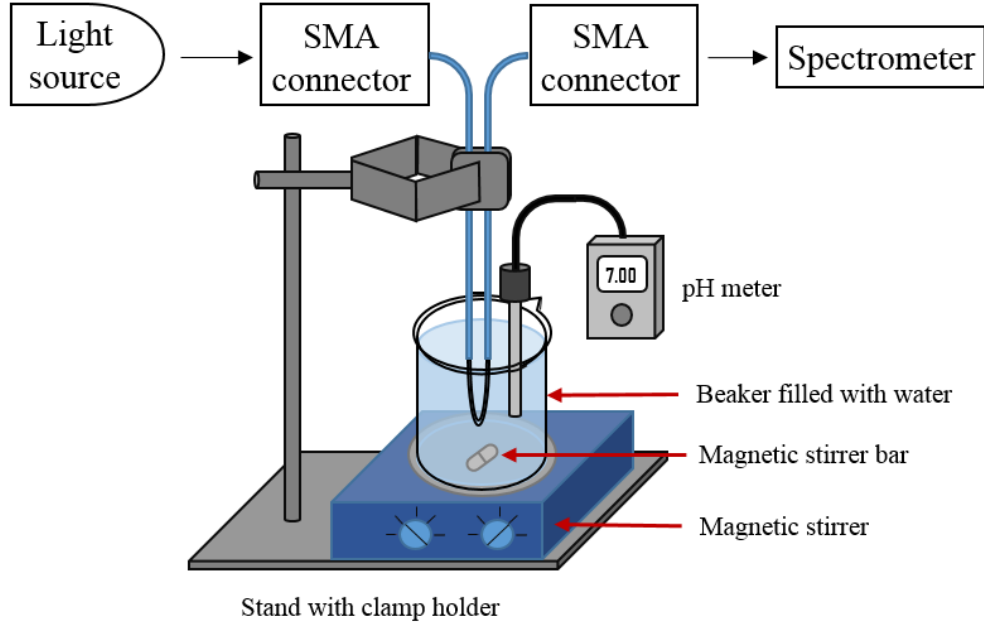


Figure 4.4: Set-up for pH measurements with optical fibre pH sensor and a commercial electronic pH meter.

4.5 Results

4.5.1 Sensor fabrication

To investigate the relationship between sensitivity and bending radius of a U-shape optical fibre, a set of fibres with bending radius from 1.5mm - 0.5mm were immersed in solutions with a range of 20% - 60% EtOH in water. The optical fibre works as a refractometer since the increment in EtOH increases the solution refractive index [217] which produces a decrease in light transmittance [218, 219, 220]. Transmittance changes in the spectra can be easily observed at the peak intensity wavelength. In this case, Figure 4.5 illustrates the transmittance changes observed at peak intensity of the spectra ($\lambda = 611\text{nm}$) for different EtOH concentrations as function of bending radii.

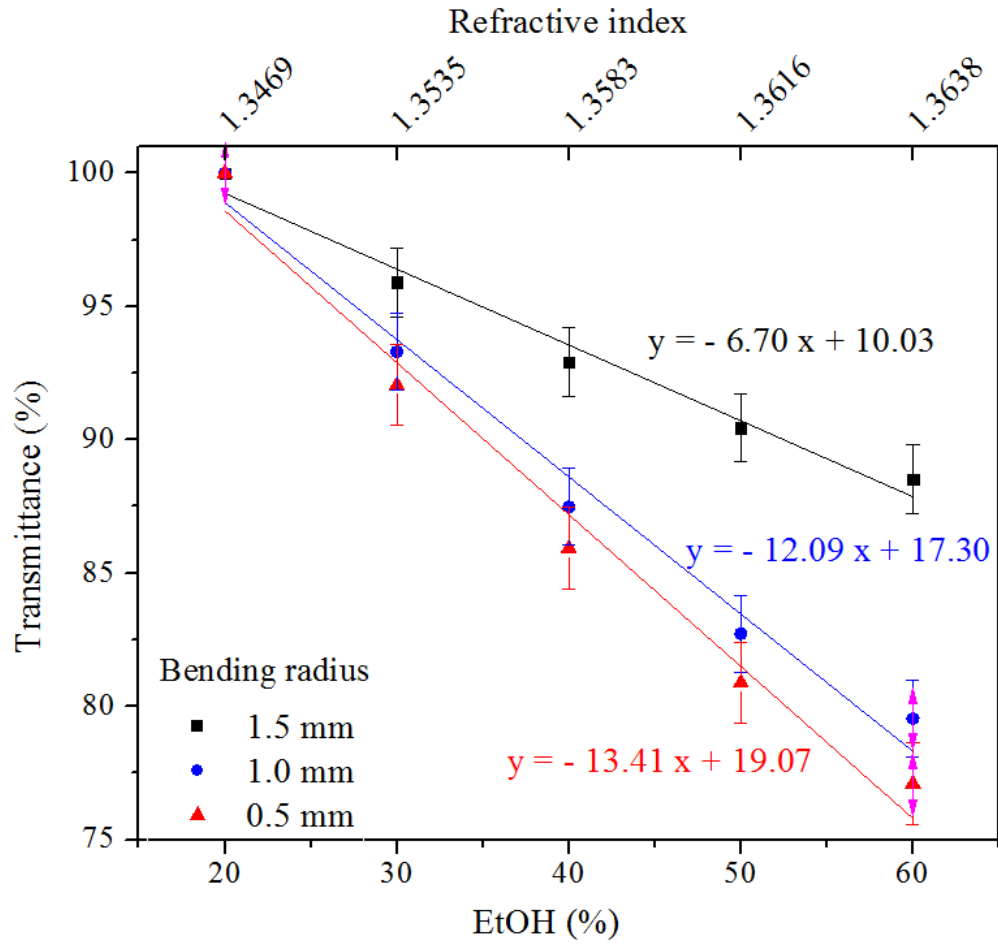


Figure 4.5: Sensitivity obtained for U-shape bending radii from 1.5mm - 0.5mm under refractive index increment of EtOH solution in water at concentration range from 20% - 60%. The transmittance changes are monitored at the peak intensity of the spectra ($\lambda = 611\text{nm}$).

It can be observed that the bending radius of 0.5mm is more sensitive to the refractive index increment in the solution since lower transmittance was obtained for high concentration of EtOH. The linear response shows a sensitivity of -13.41 in transmittance percentage per refractive index unit which corresponds to the EtOH concentration range of 20% - 60%. Therefore, the relationship between the bending radius and the sensitivity is demonstrated [185].

Additional to this, for the pH sensitive film coating two withdrawal speed were chosen to compare film thickness with the spectra obtained for the U-shape fibre with 0.5mm bending radius. Figure 4.6 shows the spectra before the film coating (optical fibre in air, black trace) and after the fibre was immersed in the sol-gel and withdrawn at 1mm.s^{-1} and 6mm.s^{-1} (red and blue trace, respectively). A

withdrawal speed of 1mm.s^{-1} produced higher absorption in the spectra (in particular at wavelengths around 500nm and 700nm), which denotes a thin coating with high concentration [139].

Moreover, Figure 4.7 highlights the absorbance spectra after the sol-gel film was coated onto the U-shape optical fibre (0.5mm bending radius, 1mm.s^{-1} withdrawal speed). It can be observed absorbance peaks at 430nm and 491nm wavelengths, which correspond to the Soret band, and at 711nm wavelength, which is characteristic to the Q band. However, it can also be noticed that these absorption bands are red-shifted, i.e., moved towards longer wavelengths compared to the Soret and Q bands from the spectra of TSPP solution in water (413nm and 645nm for Soret and Q band, respectively) [206, 221]. This wavelength-shift can be explained due to the formation of J-aggregates of TSPP in the film [213, 222, 223, 224].

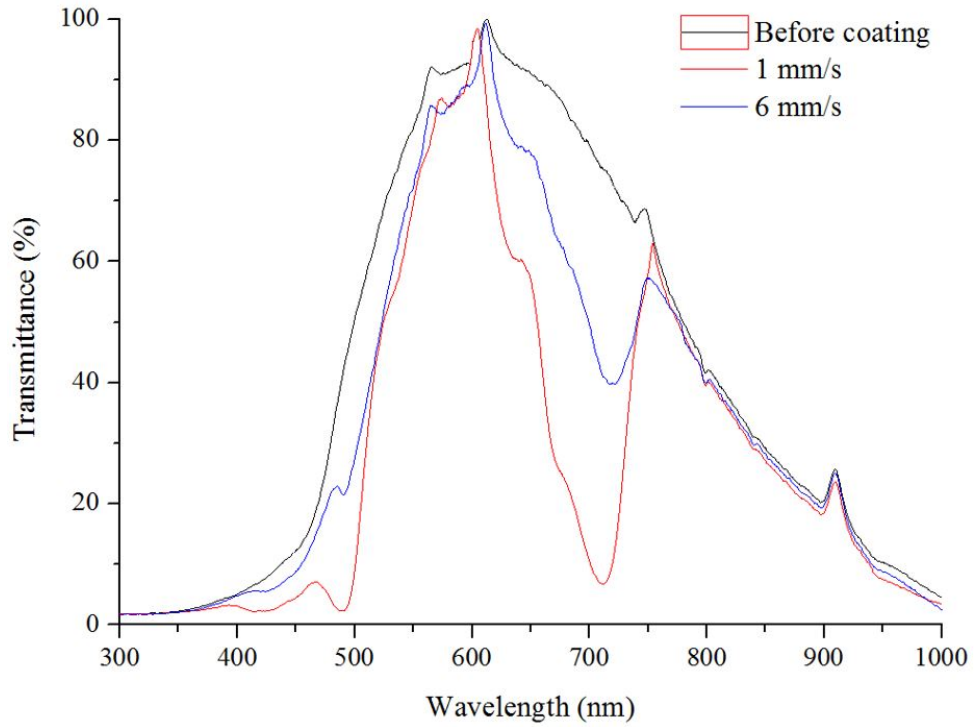


Figure 4.6: U-shape optical fibre spectra after film deposition at different dip-coating withdrawal speed, 1mm.s^{-1} (red trace) and 6mm.s^{-1} (blue trace).

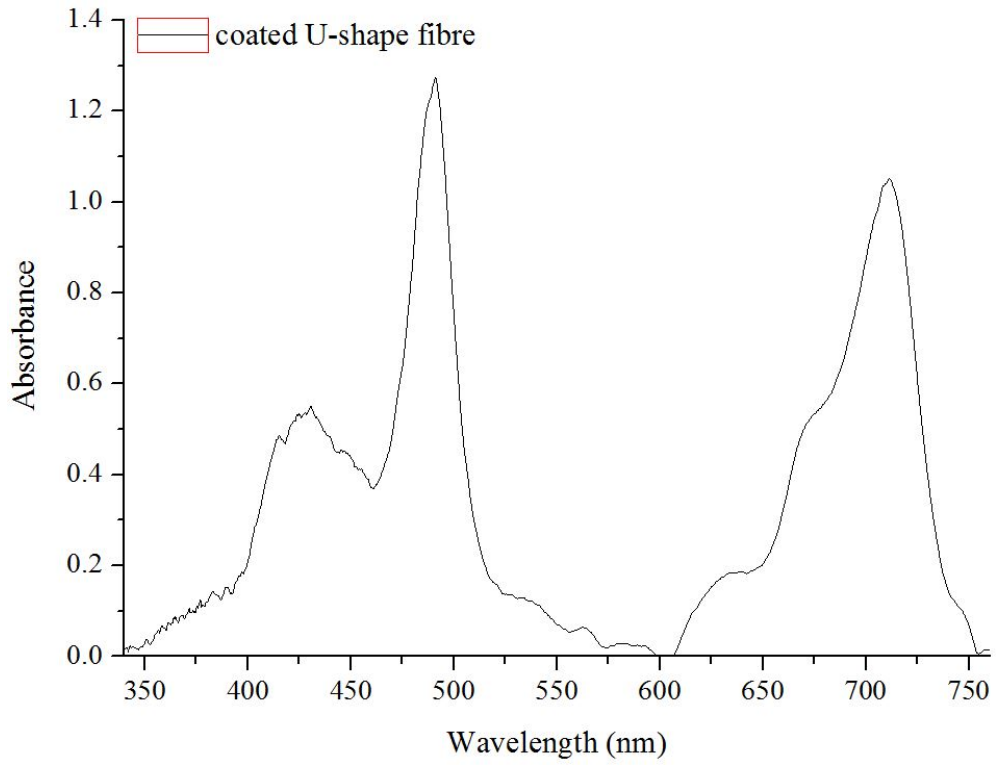


Figure 4.7: Soret and Q bands obtained after pH sensitive film coating onto U-shape optical fibre (0.5mm bending radius, withdrawal speed of 1mm.s^{-1}).

4.5.2 pH measurement

Section 4.4 illustrated the set-up for the measurement of pH with the optical fibre pH sensor. As mentioned above, after the film coating two peaks at Soret band and a peak in the Q band were produced, however, to further observe the absorbance changes in these wavelengths the spectrometer integration time was increased to 100ms in order to allow more photons to enter the spectrometer detector. Figure 4.8 shows the spectra obtained during the pH test for the range of 6.73 - 7.28 pH in the Soret band region. It can be noticed the increment in absorbance as the pH increases.

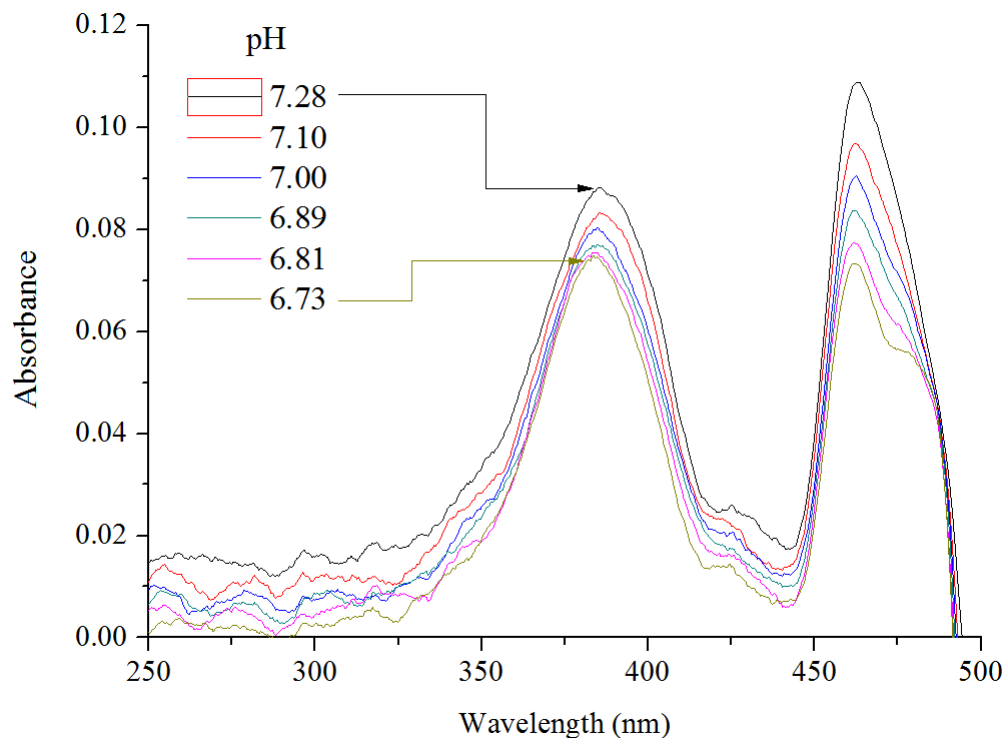


Figure 4.8: Absorbance spectra in the Soret band for the pH range from 6.73 - 7.28. Two absorbance peaks were recorded at 385nm and 461nm using a U-shape fibre with 0.5mm bending radius and 1mm.s^{-1} withdrawal speed.

On the other hand, the absorbance spectra recorded for the Q band over the same pH range is shown in Figure 4.9. The absorption change in the Q band behaves in the opposite direction to the Soret band, i.e., the absorbance decreases as the pH increases. The response of both absorption bands is caused by the protonation and deprotonation of the TSPP pyrrole ring according to the pH level in the solution [225, 226, 227].

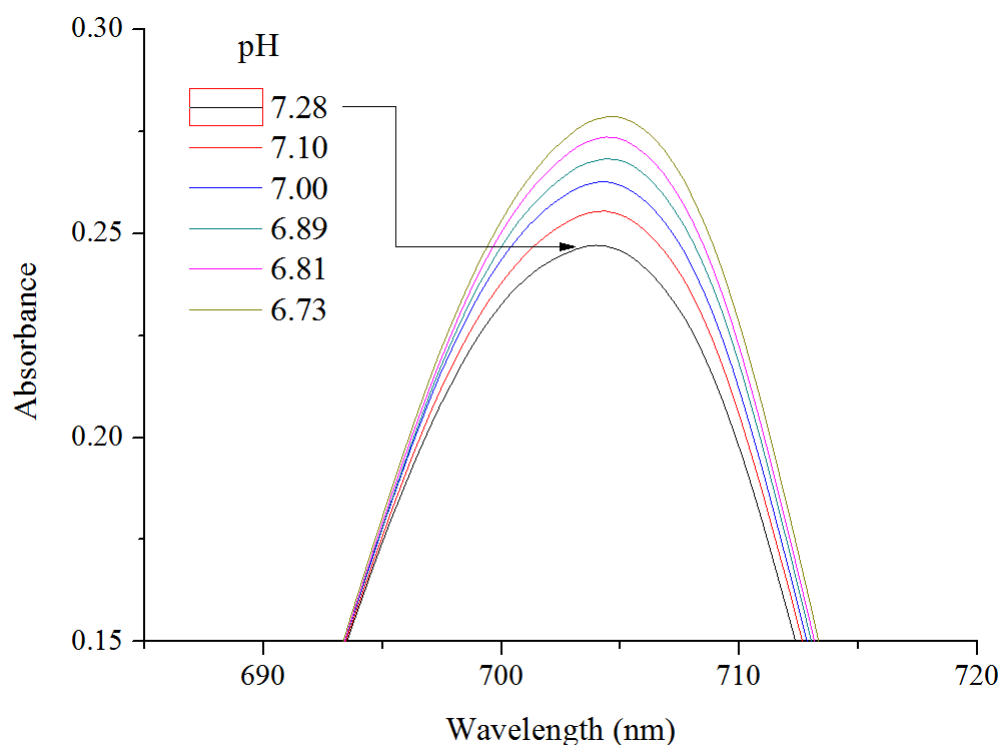


Figure 4.9: Absorbance spectra in the Q band for the pH range from 6.73 - 7.28. The absorbance peak was recorded at 703nm.

Moreover, the breadth of the range of the dynamic response of the optical fibre pH sensor was also observed by using the same set-up. Here, the pH was increased from 6.72 to 8.16. Spectra in the Soret and Q bands were recorded every second and pH was modified once the signal stabilized (~ 2.5 min). Figure 4.10 depicts the optical fibre pH sensor performance under dynamic pH change as a function of experiment time for both absorption bands.

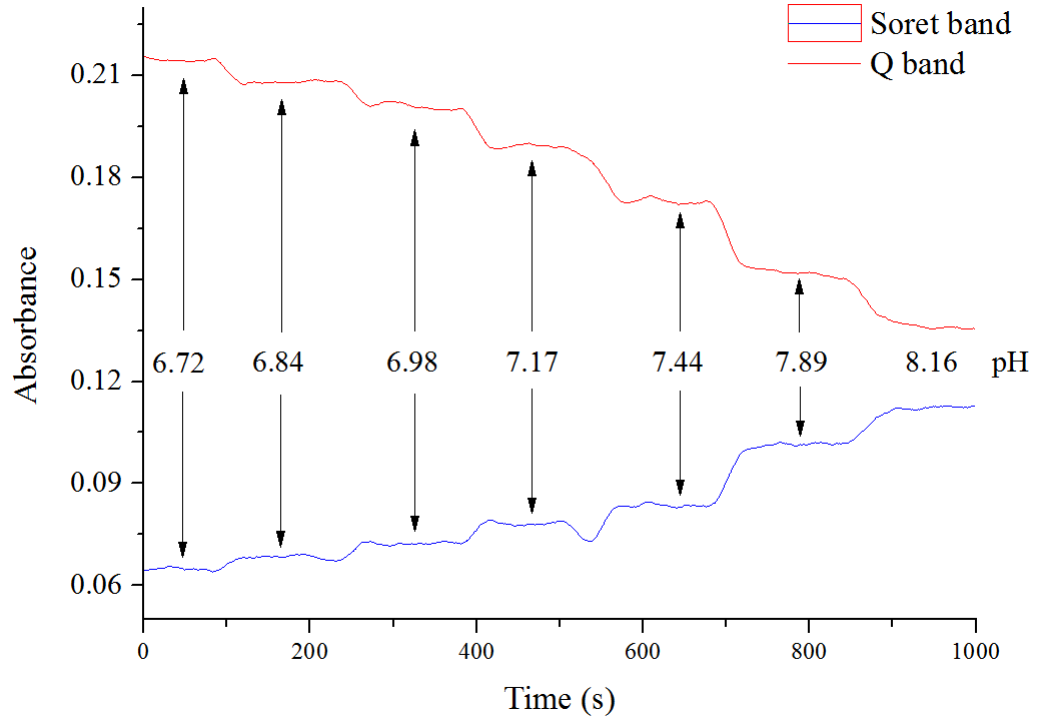


Figure 4.10: Dynamic pH measurement with optical fibre pH sensor. Soret and Q absorption bands recorded for the pH range of 6.72 - 8.16.

Furthermore, the calibration curve illustrated in Figure 4.11 shows a linear response in both absorption bands with a sensitivity of 0.032 in absorbance units per pH unit and -0.054 in absorbance unit per pH units for the Soret and Q band, respectively, for the pH range of 6.72 - 8.16. The error bars show the measurement comparison of a set of multiple optical fibre pH sensors to observe repeatability.

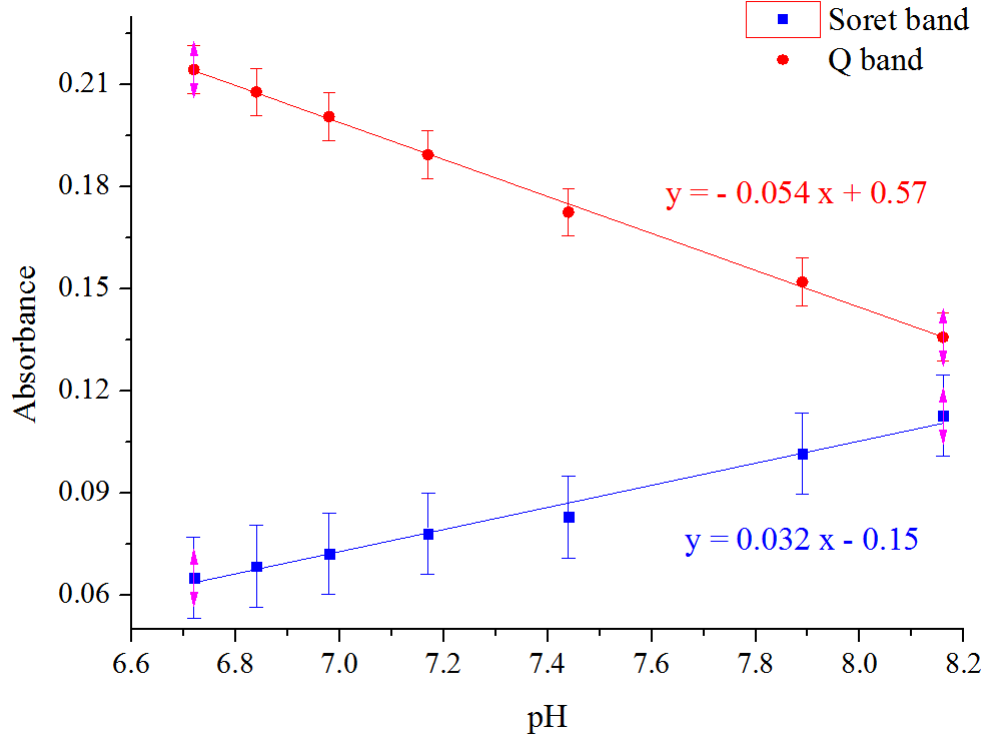


Figure 4.11: Optical fibre pH sensor calibration curve. The sensitivity achieved was 0.032 in absorbance units per pH units and -0.054 in absorbance units per pH units for the Soret and Q band, respectively, for the pH range of 6.72 - 8.16. Error bars show the comparison of a set of multiple optical fibre pH sensors to observe repeatability of measurements.

Once the sensitivity was calculated, another pH test was carried out to observe the optical fibre pH sensor response time using the same set-up. The calibration curve was used to convert the absorbance values into pH units. This test was performed in three parts:

First part: the pH was increased from 7.05 to 7.30 by continuously adding NaOH in a dropwise fashion.

Second part: the pH was rapidly decreased by pouring 80 μ L of HCl to the solution. The pH recorded after the acid addition was 6.74.

Third part: NaOH was added once again to observe repeatability in the measurements until reaching the initial pH value of 7.05.

The Soret and Q band behaviour in real-time of the optical fibre was compared with the values obtained from the commercial pH meter electrode and the results are illustrated in Figure 4.12.

The Soret band (blue trace) shows a noisy signal during the first part of the experiment (before adding HCl to decrease pH). This corresponds to the low light intensity detected by the spectrometer, as illustrated in Figure 4.6 in the Soret band region. According to the calibration curve (Figure 4.11, blue trace) the pH change is proportional to the absorbance in the Soret band, i.e. when the pH increases the absorbance also increases. Therefore, when the pH is increased from 7.05 to 7.30 (first part), the absorbance increases, hence the light intensity at the end of the OFS is difficult to be detected by the spectrometer, unless the spectrometer integration time is further increased. Next, when the pH is decreased during the second part of the experiment (i.e., pouring acid into the solution) the absorbance decreases as well, hence the light intensity detected by the spectrometer is more noticeable. As the third part is carried out (i.e., pouring alkali into the solution) the signal to noise ratio (SNR) has now increased and the response is similar to that obtained from the commercial pH meter electrode (green trace).

On the other hand, the light intensity recorded at the Q band (red trace) is higher than that from the Soret band as illustrated in Figure 4.6, therefore, the pH changes can be easily detected by the spectrometer. The Q band shows a similar response to that observed with the commercial pH meter electrode (green trace).

Finally, the rapid decrease in pH during the second part of the test was deployed (using the Q band) in order to obtain the sensor response time. This was found to be 33s and 42s for the pH meter electrode and the optical fibre pH sensor, respectively.

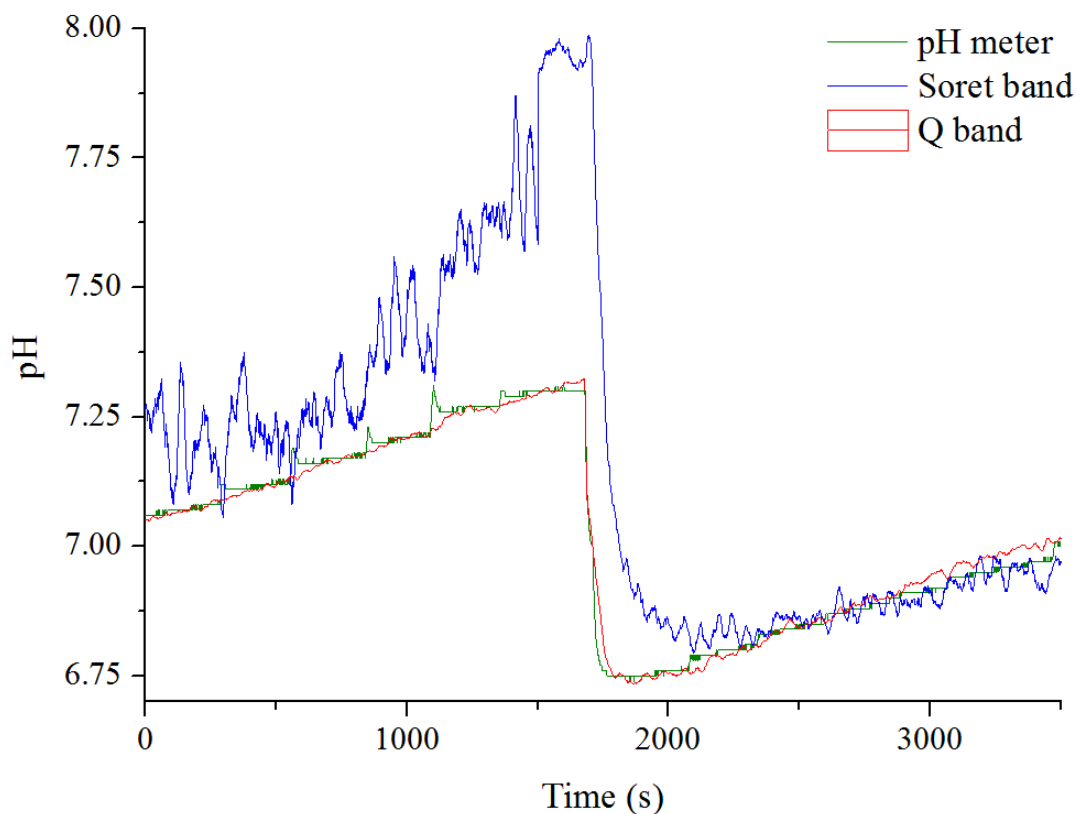


Figure 4.12: Real-time pH measurements in the Soret and Q band. HCl and NaOH were added to the solution to modify the pH. The optical fibre pH sensor response was compared with a commercial pH meter electrode.

4.6 Summary and comments

In this chapter, the development of a pH sensor based on a U-shape optical fibre coated with a sol-gel film containing TSPP as a pH indicator was described.

The spectra characteristics of the sensor were studied. Absorbance bands were found in the Soret and Q region of the visible spectra. The response of both absorption bands was tested over a pH range from 6.72 - 8.16. The sensitivity obtained was 0.032 in absorbance units per pH unit and -0.054 in absorbance units per pH units for the Soret and Q band, respectively.

Measurements of pH in real-time were compared between the optical fibre pH sensor and a commercial pH meter electrode showing similar response with both

sensors. The response time observed with the OFS was 42s due to a rapid change in pH compared to 33s for the commercial pH sensor.

Future work will include an investigation over the durability and leachability of the sensitive film. The use of a surface active reagent, as reported in [132] can be useful to increase the sensor durability and reduce leaching rate.

Moreover, although the experimental set-up (Figure 4.4) produced pH variations of 2 decimal places, further experiments with pH buffers with such small pH variation are yet to be made in order to observe the OFS resolution. In addition, it is important to highlight the importance of a highly sensitive detector for the evaluation system to improve the SNR in the OFS Soret band.

The results obtained with the optical fibre pH sensor developed demonstrate a real potential for deployment in medical settings where the detection of small pH changes and a relatively fast response is crucial. One example is during foetal blood sampling to provide more information to clinicians in-situ in order to decide whether an intervention is necessary in newborn delivery.

Chapter 5

Electronic Portable Evaluation System

*"Equipped with his five senses, man explores the universe around him and calls
the adventure Science."*

- Edwin Powell Hubble -

5.1 Introduction

In the previous two chapters the development of two OFSs for humidity and pH measurements were described. The evaluation system used to monitor the response of both sensors consisted of a halogen light source which sends light through the OFS and a spectrometer to collect the resultant optical signal from the interaction between the environment and the sensitive region. The spectrometer output signal can be observed in a computer through specific software (Spectra suite, Ocean optics, Ltd.).

The experimental evaluation system was useful for monitoring the fabrication of the sensors, laboratory experiments and the sensors characterization. However, this evaluation system is expensive ($\sim$ £2,800 and £1,200 for the halogen light source and the spectrometer, respectively) and requires special treatment since the components can be damaged by rough handling or under hazardous environments such as the bulb from the light source and the alignment of the slit in the spectrometer. Most importantly, these devices are not compatible with ambulatory monitoring.

The design of a portable evaluation system is crucial for the objectives and motivation of this PhD (described in Section 1.8). For example, in Section 3.7 the POFHS embedded within a wound dressing provided promising results for humidity measurements on the skin. The use of a portable device to recover the POFHS signal can be advantageous to obtain remote, continual measurements and provide comfort to either patients (for wound healing monitoring) or athletes (for sport activities) due to the small size that can be achieved.

In the case of pH measurements the implementation of a portable device can be of benefit to clinicians for pH measurements during foetal blood sampling (FBS) since the analysis of the sample can be performed in the labour and delivery suite. Therefore the time normally spent in carrying the sample to a laboratory can be reduced and hence a prompt decision can be taken for the newborn delivery.

In this chapter, the design of a cost-effective and portable OFS evaluation system

is described. The experimental set-up based on a halogen light source and a spectrometer is replaced by an LED and a photo-diode, respectively. An operational amplifier in the transimpedance configuration is used to convert the photo-diode current into voltage. Digitisation of the signal is carried out by an analog-to-digital converter (ADC) to be further processed by a microcontroller. The data obtained is then stored in a secure digital (SD) memory card and is wirelessly transmitted in real-time to a computer via Bluetooth.

5.2 OFS evaluation system design

5.2.1 Light source

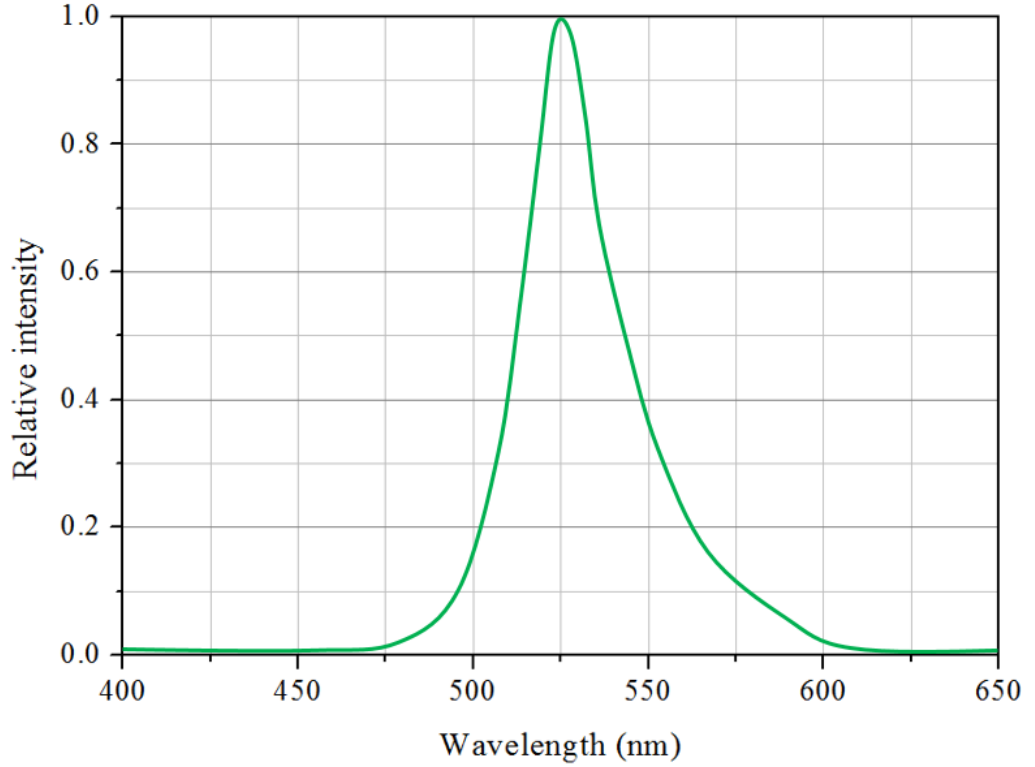
The first part of the optical evaluation system is the light source that will launch light into the OFS. As explained in Section 1.6, two main types of light sources exist: the LED and the laser. In this project, for the development of the OFS evaluation system, an LED was selected due to the small size and simple driver circuit required for its operation.

In order to select the appropriate LED, some characteristics were required namely: luminous intensity; forward voltage; forward current; dominant wavelength; and package or encapsulation. A relatively low light level is reflected from the OFS sensing region, therefore it is important to launch light with high luminous intensity in order to observe easily the attenuation of light. The dominant wavelength required is based on the OFS characteristics. In the case of the POFHS, attenuation of light can be monitored at any wavelength in the visible spectrum. The chosen LED that fulfills these parameters was the HLMP-CM1A-560DD manufactured by Avago Technologies. The characteristics of this LED are listed in Table 5.1.

Table 5.1: HLMP-CM1A-560DD LED parameters.

Parameter	Symbol	Min.	Typical	Max.	Unit
Forward voltage	V_f	2.8	3.2	3.8	V
Forward current	I_f	-	-	30	mA
Luminous intensity	I_v	45000	60500	76000	mcd
Dominant wavelength	λ_d	519	525	539	nm

The spectrum of the selected LED shows a dominant wavelength at 525nm (Figure 5.1). This monochromatic LED (green) has a 5mm clear encapsulation which can be mounted into a bulk head SMA connector to enhance light coupling into the OFS with minimal losses.

**Figure 5.1:** Spectra of the HLMP-CM1A-560DD LED. Dominant wavelength = 525nm.

Conversely, the OFS for pH measurements absorbs light at specific wavelengths, as described in Section 4.5.2. The LED dominant wavelengths for this sensor are based on the Soret and Q bands of the spectra ($\sim 500\text{nm}$ and $\sim 700\text{nm}$, respectively). Further work will include the selection of the appropriate light source to monitor pH measurements in the Soret and Q absorbance bands.

5.2.2 Detector

Section 1.6 also explains that the purpose of a photo-detector is to efficiently convert the small amount of light from the OFS into electrical current. The photo-detector selected for the evaluation system was a photo-diode due to its low-cost, high sensitivity to a narrow wavelength range and small size. The photo-diode will play an important role within the evaluation system to detect the optical signal from the OFS and to produce an electrical current proportional to the incident light which will be sent to the next stage of the evaluation system.

There are three main requirements to ponder for the photo-diode namely: high sensitivity at the wavelength propagated through the OFS (in this case, 525nm wavelength); fast rise and fall time; low dark current; and high shunt resistance.

As explained in Section 1.6, the materials of the photo-diode will define its sensitivity at a given wavelength. The timing response will depend on the photo-diode junction capacitance, C_j : the lower the capacitance the higher operation speed. In addition, since small light intensity changes are required to be detected, the photo-diode will be used in the photo-voltaic configuration, therefore the photo-diode must have a very low dark current in order to avoid masking the photo-current with the noise equivalent power (NEP, Section 1.6).

The photo-diode selected was the BPW21R manufactured by Vishay Ltd. This photo-diode has the following characteristics (Table 5.2):

Table 5.2: BPW21R photo-diode characteristics.

Parameter	Symbol	Min.	Typical	Max.	Unit
Dark current	I_d	-	2	30	nA
Shunt resistance	R_{sh}	-	38	-	$G\Omega$
Spectral range	λ	400	565	750	nm
Responsivity $\lambda=525\text{nm}$	R	-	0.25	-	A/W
Rise time	t_r	-	3.1	-	μs
Fall time	t_f	-	3.0	-	μs

The photo-diode has a TO-5 package, which can be fixed within a bulk head SMA connector to receive the OFS signal reducing losses and ambient light disturbance in the desired optical signal. However, noise in the signal will be produced by the photo-diode, as explained in Section 1.6.

The shot and thermal noise sources for this photo-diode at 25°C can be calculated using the Equations 1.9 and 1.10:

$$i_{sh} = \sqrt{2(1.6 \times 10^{-19}C)(2 \times 10^{-9}A)} = 25.29fA/\sqrt{Hz} \quad (5.1)$$

And,

$$i_{th} = \sqrt{\frac{4(1.38 \times 10^{-23}J.K^{-1})(298.15K)}{38 \times 10^9\Omega}} = 0.66fA/\sqrt{Hz} \quad (5.2)$$

Hence the current noise produced by the photo-diode calculated by Equation 1.11 is:

$$i_{tot} = \sqrt{(25.29 \times 10^{-15}A)^2 + (0.66 \times 10^{-15}A)^2} = 25.29fA/\sqrt{Hz} \quad (5.3)$$

Therefore, using Equation 1.12 the NEP at 525nm wavelength can be calculated:

$$NEP = \frac{25.29 \times 10^{-15}A/\sqrt{Hz}}{0.25A/W} = 0.1pW/\sqrt{Hz} \quad (5.4)$$

The output optical power from the OFS was observed by connecting the selected LED and a digital power meter (PM100 digital optical power meter, S120B silicon sensor, spectral range 400nm - 1100nm, 100pW resolution, Thorlabs Ltd.) to each end of the OFS. The output power observed was in the range of nano-Watts, therefore, the photo-diode is suitable for detection of the OFS optical signal.

The photo-diode is connected to a transimpedance amplifier (TIA) in order to convert the photo-current into voltage. There are several characteristics to be considered in order to select an appropriate op-amp, some of them are: input bias current; input impedance; and input-referred voltage and current noise. These characteristics are observed to obtain a low output noise.

In this case, the LMC662-AI operational amplifier manufactured by Texas Instruments was selected. This dual op-amp produced with complementary metal-oxide semiconductor (CMOS) technology has the following characteristics (Table 5.3):

Table 5.3: LMC662-AI operational amplifier characteristics.

Parameter	Typ.	Max.	Unit
Operating range	5	15	V
Input bias current	0.002	4	pA
Input resistance	>1	-	TΩ
Gain-bandwidth product	1.4	-	MHz
Input-referred voltage noise (f = 1kHz)	22	-	nV/ $\sqrt{Hz}$
Input-referred current noise (f = 1kHz)	0.0002	-	pA/ $\sqrt{Hz}$

Figure 5.2 shows the circuit diagram for the conversion of the optical signal into voltage. The output voltage depends on the photo-current and the feedback resistance, as expressed in Equation 1.13. However, special attention must be given to the noise sources presented in Section 1.6.

The current shot noise can be calculated using Equation 1.14 for a given DC photo-current of 100nA:

$$i_{sh} = \sqrt{2(1.6 \times 10^{-19}C)(100 \times 10^{-9}A)} = 0.17pA/\sqrt{Hz} \quad (5.5)$$

According to Equation 1.13, a feedback resistor with high value is required to increase the gain. In this project a feedback resistor of $10\text{M}\Omega$ was used due to the small photo-current obtained. Therefore the voltage shot noise is calculated using Equation 1.15:

$$V_{sh} = (0.17 \times 10^{-12}\text{A})(10 \times 10^6\Omega) = 1.7\mu\text{V}/\sqrt{\text{Hz}} \quad (5.6)$$

Moreover, the thermal noise due to the feedback resistor at 25°C is calculated using Equation 1.16:

$$V_{th}Rf_{(rms)} = \sqrt{4(1.38 \times 10^{-23}\text{J.K}^{-1})(298.15\text{K})(10 \times 10^6\Omega)} = 0.41\mu\text{V}/\sqrt{\text{Hz}} \quad (5.7)$$

The voltage noise (e_n) and current noise (i_n) obtained from the op-amp manufacturer's datasheet are $22\text{ nV}/\sqrt{\text{Hz}}$ and $0.2\text{ fA}/\sqrt{\text{Hz}}$, respectively at 1kHz . Following Equation 1.17:

$$V_n = (0.2 \times 10^{-15}\text{A})(10 \times 10^6\Omega) = 2\text{nV}/\sqrt{\text{Hz}} \quad (5.8)$$

Therefore, the total op-amp output voltage noise can be expressed using Equation 1.18:

$$\begin{aligned} V_{nT} &= \sqrt{(1.7 \times 10^{-6})^2 + (0.41 \times 10^{-6})^2 + (22 \times 10^{-9})^2 + (2 \times 10^{-9})^2} \\ V_{nT} &= 1.74\mu\text{V}/\sqrt{\text{Hz}} \end{aligned} \quad (5.9)$$

The op-amp output is connected to a low-pass filter (LPF) consisting of the arrangement of a resistor and a capacitor in order to set an anti-aliasing filter. The resistor and the capacitor values of $16\text{k}\Omega$ and $10\mu\text{F}$, respectively were selected to set the LPF cut-off frequency to 1Hz . The cut-off frequency was set according to the sensor response time observed which are 1.5s and 42s for the humidity and the pH OFSs, respectively. The next section explains the further stages in the OFS evaluation system.

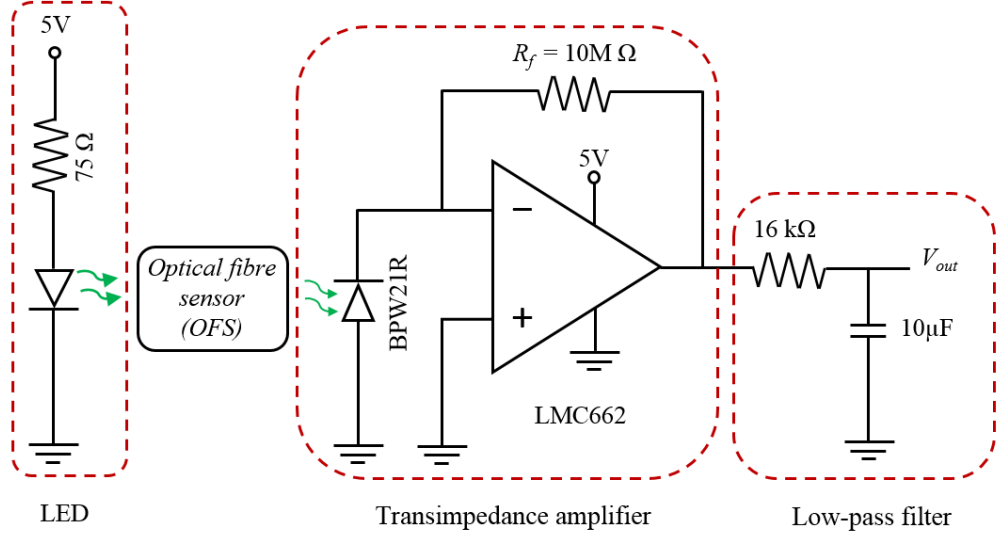


Figure 5.2: Circuit diagram for optical signal conversion into voltage.

5.2.3 Data processing

The next stage of the OFS evaluation system is the digitisation of the output signal. An analog-to-digital converter (ADC) is a useful device that can transform the analog output voltage from the TIA into a digital value from a set scale. The ADC used in this work is the ADS1115 manufactured by Texas Instruments. This is a 16-bit ADC that can perform data conversions at a rate from 8 - 860 samples per second (sps). The sampling rate selected was 10sps based on the Nyquist theorem which establishes that the sampling rate must be at least twice the signal frequency to be measured. Moreover, the minimum voltage that can be digitalized by the ADC is known as the least significant bit (LSB), which can be calculated using Equation 5.10:

$$LSB = \frac{V_{ref}}{2^n} \quad (5.10)$$

Where V_{ref} is the voltage reference and n is the ADC resolution or number of bits (in this case 16 bits). Therefore, for a given voltage reference of 5V, the smallest measurement that the ADC can perform is $76.29\mu V$. It is important that the LSB has a higher value than the circuit noise without compromising the sampling resolution (Nyquist theorem). In this project the LSB from the 16-bit ADC is higher than the voltage noise from the TIA, hence measurements with

high resolution can be obtained above the noise level.

Once that the TIA signal has been digitized, the output data is sent to a microcontroller in order to be further processed. The microcontroller used was the ATmega328P created by Atmel. This microcontroller was used to convert the measured intensity into the required parameter (humidity or pH) according to a code written in C programming language (Appendix A) containing the calibration curve values from the OFS developed.

The last stage of the OFS evaluation system is the data transmission. The microcontroller output data is transmitted via wireless to a computer using a Bluetooth module. The module used was the Bluetooth Mate silver (SparkFun Electronics Ltd.). This low-power consumption (25mA) module can stream data at a range from 2400 - 115200 bits per second (bps). It features a Class 2 Bluetooth IC (RN-42) with a built-in antenna which provides a transmission radio of 20m.

Simultaneously, the data is also sent to a micro-SD card as a back-up storage in case the wireless transmission experiences issues, for example, data transmission out of range. A low power consumption module (5 - 6mA idle current draw, 20 - 23mA active writing current draw, OpenLog data logger, Sparkfun Electronics Ltd.) was used to save the data in a 4GB micro-SD card. Serial communication was used to associate the microcontroller with both the Bluetooth and the SD card module.

5.3 PCB design and manufacturing

The previous sections determined the components required for the electronic circuit in the evaluation system. The circuit operation was tested initially in a bread board. However, in order to provide the OFS evaluation system with reliable portability for practical applications a small and thin electronic circuit is required, hence a printed circuit board (PCB) was designed.

The PCB layout was designed with the aid of the software "EAGLE" ver. 8.1.0

from Autodesk Inc (Appendix B). This software is a schematic editor for designing circuit diagrams and PCBs. The developed circuit board consists of 2 layers (i.e., component placement on both sides of the board. Appendix C). The manufacturing and the assembling of the SMD electronic components onto the PCB was made by an external company (PCB Train, Newbury Electronics Ltd, UK.). Figure 5.3 displays both faces of the developed PCB for the OFS evaluation system. The dimensions of the PCB are 45mm length and 35mm width. The thickness of the PCB including the modules for the SD card, the ADC and the Bluetooth is 12mm.

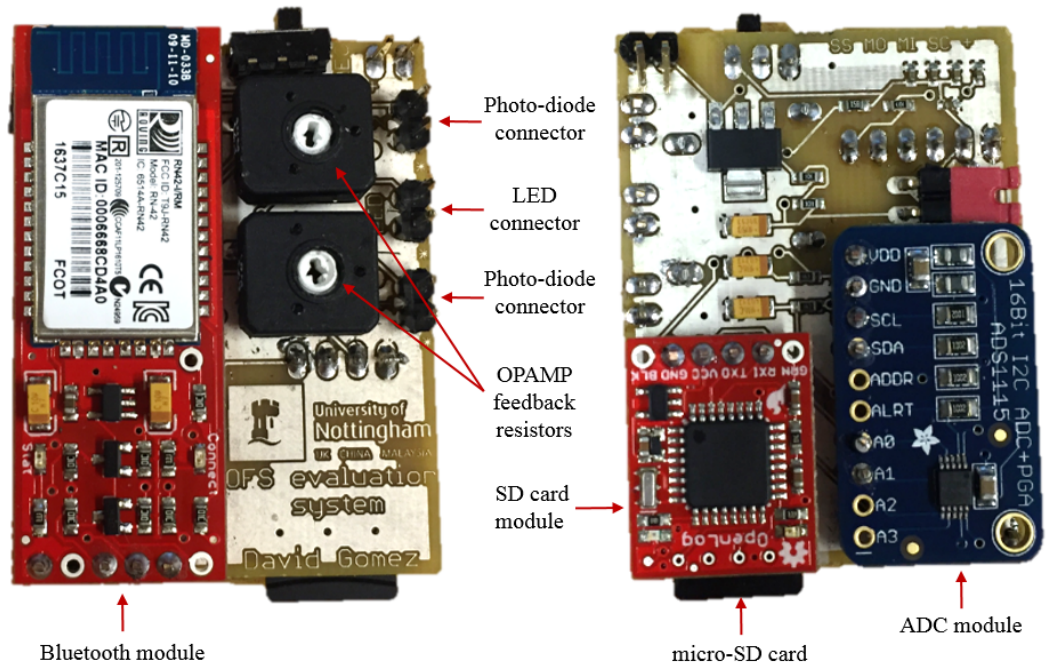


Figure 5.3: OFS evaluation system PCB. Top view (left) and bottom view (right).

Some key components are shown in Figure 5.3 namely: the photo-diode and LED connectors; the modules for the ADC, Bluetooth and SD card; and the potentiometers used for the transimpedance amplifier feedback resistor. Additional components such as the microcontroller and the op-amp used are located under the Bluetooth module due to its size and thickness (thin quad flat package, TQFP for the microcontroller and small-outline integrated circuit package, 8-SOIC for the op-amp).

One of the most important pillars in the development of a new device is the cost-

effectiveness. Table 5.4 depicts the total cost for the electronic components of the OFS evaluation system.

Table 5.4: OFS evaluation system electronic components cost.

Component	Value or model	Qty.	Cost
Microcontroller	ATmega328P	1	£1.55
Resonator	16MHz	1	£0.30
op-amp	LMC662AIN	1	£1.10
Capacitor	0.1 μ F, 1 μ F, 10 μ F	8	£0.50
Resistor	75 Ω , 100 Ω , 300 Ω , 10k Ω , 16k Ω	6	£1.30
Voltage regulator	LM317	1	£0.55
Potentiometer	10M Ω	2	£1.25
Slide switch	-	1	£0.40
Pin headers	-	32	£2.50
16-bit ADC	ADS1115	1	£1.25
Bluetooth module	Mate silver	1	£17.50
SD card module	Openlog	1	£10.50
MicroSD card	4GB	1	£5.50
LiPo Battery	3.7V, 400mAh	2	£7.50
LED	HLMP-CM1A-560DD	1	£0.30
Photo-diode	BPW21R	2	£15.00
Total cost			£67.00

Moreover, there are some additional costs for the operation of the OFS evaluation system namely: the PCB fabrication; the SMA connectors; and the SMA bulkhead receptacle. Table 5.5 shows the cost of these components:

Table 5.5: OFS evaluation system additional components cost.

Item	Qty.	Cost
PCB fabrication	1	£106.50
SMA bulkhead receptacle	3	£40.50
SMA fibre optic connector	3	£18.00
Total cost		£165.00

It is important to notice that this cost is for the development of a single unit of the OFS evaluation system, therefore, the total cost for the electronic components, the PCB manufacturing and the optical connectors will decrease for a mass production. As part of the future work in this project, some components can be minimized. For example, the SD card and the ADC modules can be replaced by an SD card socket and the IC from the ADC, respectively, connected directly to the microcontroller which can result in the PCB size reduction. Moreover, the use of different optical connectors such as the lucent connector (LC) or plastic optical connectors can further decrease the OFS evaluation system final cost.

5.4 POFHS test with OFS evaluation system

In Section 1.8 the motivation of this PhD to implement the POFHS within garments for humidity measurements on the body was described. This was to provide a more complete analysis of the body performance and improve or personalise exercise routines that can lead to a reduction in potential injuries and faster body recovery. The performance of both the OFS evaluation system and the POFHS was tested with the measurement of humidity being expelled from the body while cycling.

5.4.1 System set-up

In order to perform a humidity test on the body while cycling, the POFHS developed was placed in the evaluation system designed. Figure 5.4 illustrates the set-up for the humidity test with the POFHS and the evaluation system.

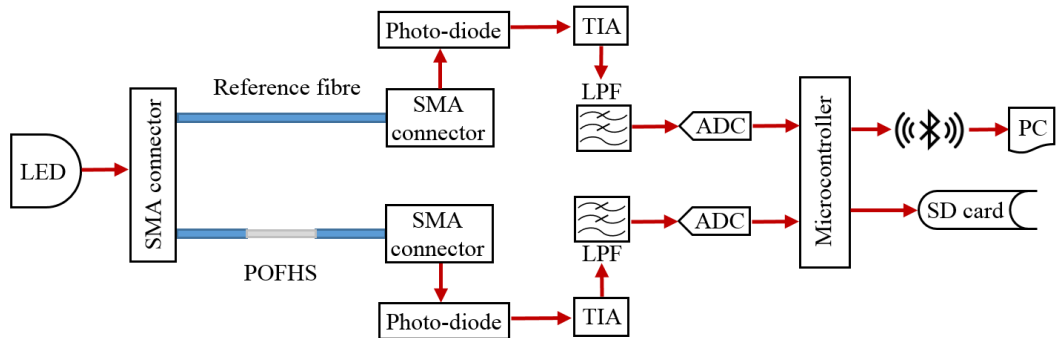


Figure 5.4: OFS evaluation system set-up for humidity measurements with POFHS.

The set-up consists of the use of a bare unmodified optical fibre as a reference for bending losses due to the motion during exercise. The reference fibre cladding is maintained in place since the humidity can affect the reference signal when the cladding is removed as observed in Figure 3.16a from Section 3.6.3. The POFHS and the reference fibre are connected to a single SMA connector at one end to receive light from the LED and at the other end to individual SMA connectors. The optical signal is collected by a photo-diode for each fibre. As mentioned in Section 5.2.2, the LMC662-AI is a dual op-amp IC, therefore both op-amps were used to collect individually each optical signal from the reference fibre and the POFHS photo-diodes.

The reference fibre and the POFHS are placed within a 3D-printed holder (dimensions 90mm length, 35mm width and 10mm thick) as shown in Figure 5.5 (left). The reference fibre is located beneath the humidity sensor in order to follow the same path as the POFHS. Both fibres are twisted to be held together outside the 3D-printed holder. The function of the holder is to reduce bending losses caused by body movements during cycling such as pedalling and leaning of the body. The 3D-printed holder features a window (dimensions: 40mm length and 7mm width) in order to locate the POFHS sensing region and avoid direct contact with the skin.

5.4.2 Method

Prior to the humidity experiment on the body while cycling, the 3D-printed holder was placed within the environmental chamber deployed in Section 3.4.1 to calibrate the POFHS. Humidity measurements were taken in the range of 50% - 90% RH with the temperature at 25°C. The humidity was cycled up and down three times. The OFS evaluation system was used to register the POFHS signal.

In addition, another humidity test was carried out to observe both the POFHS signal and the reference fibre performance over bending losses. The 3D-printed holder including the POFHS and the reference fibre was placed within the environmental chamber and humidity changes in the range of 35% - 85% were

monitored with the POFHS and the commercial capacitive humidity sensor used in Section 3.4 (iButton Hygrochron Temperature/Humidity Logger, DS1923, 0 to 100%RH, Maxim Integrated Ltd.). During the test both the POFHS and the reference fibre were manually bent on two occasions.

In order to observe the POFHS performance in sport activities, two experiments were performed. Both tests were carried out at room temperature (23°C) using an indoor exercise bike (Wattbike Pro, Wattbike Ltd., UK). The OFS evaluation system was placed on the volunteer's waist as shown in Figure 5.5 (right). Humidity measurements were taken on a single volunteer (male, healthy, age 27) wearing sports clothing. Ethical approval was provided by the Ethics Committee, Faculty of Engineering, University of Nottingham (Appendix D).

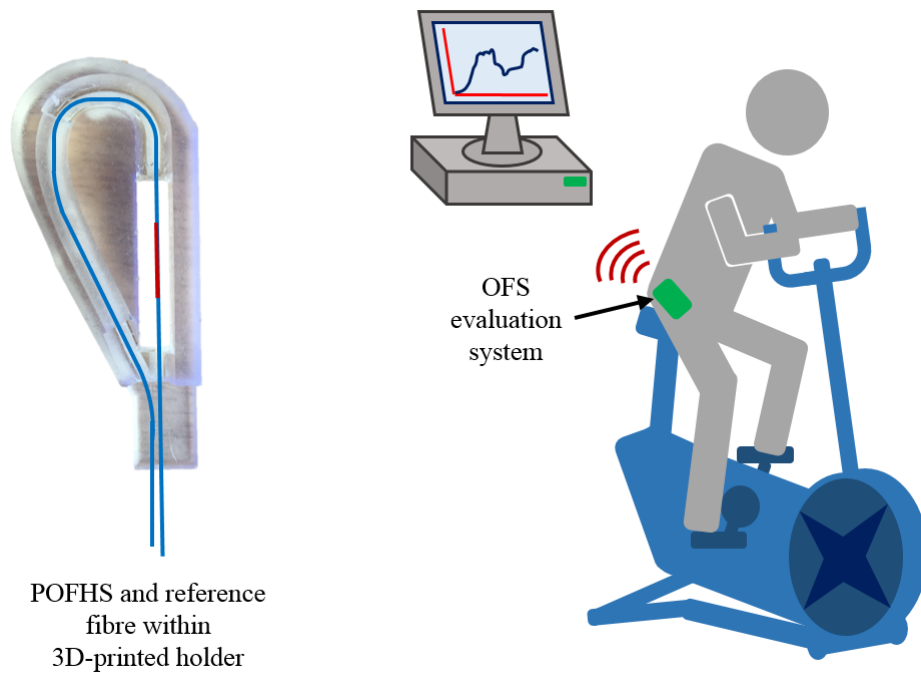


Figure 5.5: Humidity test using indoor exercise bike. The 3D-printed holder including the POFHS and the reference fibre (left) is placed on the body to measure humidity during cycling (right). The OFS evaluation system is placed on the volunteer's waist.

The first test consisted of measuring the humidity produced in the chest of the body while cycling. The 3D-printed holder containing the POFHS and the reference fibre was placed at the centre of the volunteer's chest. The commercial

humidity sensor was located next to the 3D-printed holder to compare measurements. The experimental protocol for this test was performed in collaboration with a company involved in the development of smart textile technology namely Footfalls & Heartbeats Ltd., UK. The proposed protocol was the following: 1min static position prior pedaling; 5min pedaling; and 5min static position.

In the second test the 3D-printed holder containing the POFHS and the reference fibre was placed at the centre of the volunteer's upper back. Table 5.6 describes the protocol followed for the humidity measurements at the upper back while cycling using the POFHS and the OFS evaluation system.

Table 5.6: Protocol for the humidity measurements at the upper back during cycling.

Activity	Duration
Static position	3 min
Pedaling	10 min
Stop pedaling	3 min
Pedaling	10 min
Stop pedaling	3 min
Breaths on sensor	3 min

5.4.3 Results

Prior to the humidity measurements on the body while cycling, the calibration curve of the POFHS with the evaluation system was obtained. Figure 5.6 shows the POFHS calibration curve obtained with the evaluation system for a humidity range of 50% - 90%RH measured with the environmental chamber sensor. The sensitivity achieved was 13mV/%RH.

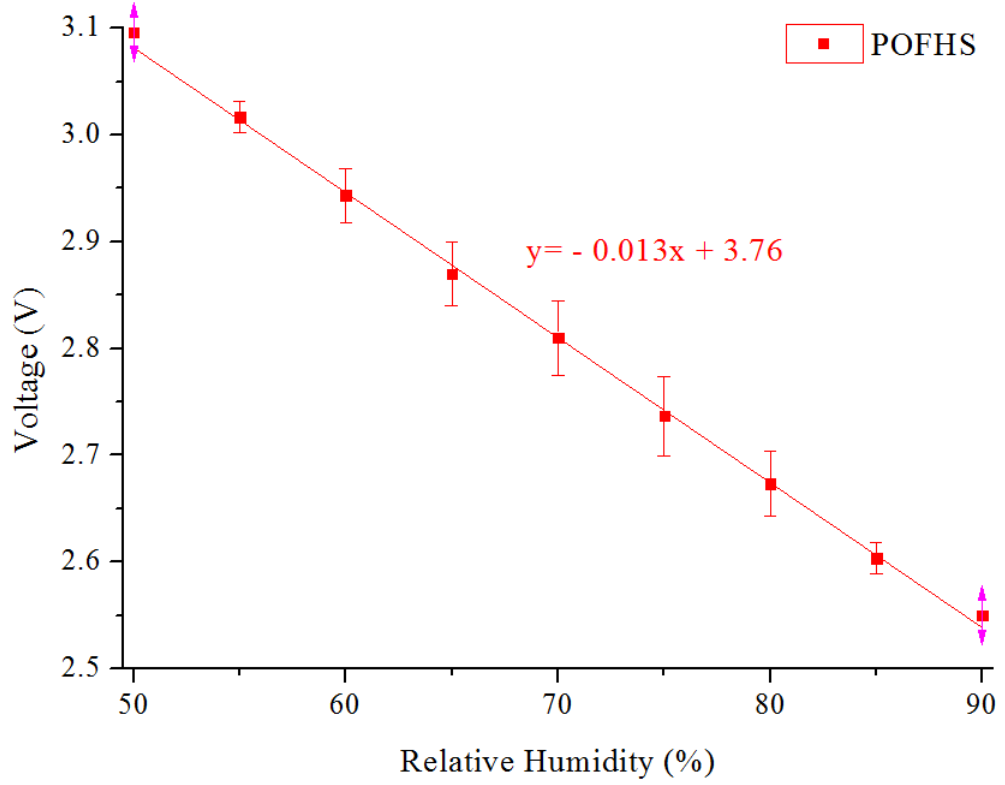


Figure 5.6: POFHS calibration curve obtained with the OFS evaluation system. The sensitivity achieved was 13mV/%RH for a range of 50% - 90%RH at 25°C.

Moreover, the deployment of a reference fibre to detect bending losses was tested with another humidity test. The purpose of this experiment was to observe the response of both the reference fibre and the POFHS over humidity variations in the range of 35% - 85% and manually created bending losses. It was expected to observe signal changes with respect to the humidity only in the POFHS whilst the detection of bending losses would be seen with both fibres. Figure 5.7 shows the POFHS (red trace) and the reference fibre (black trace) response for this experiment. The humidity measurements are compared with the commercial sensor (blue trace). Furthermore, Figure 5.8 shows a zoom in from Figure 5.7 around the first bending loss detected with both fibres.

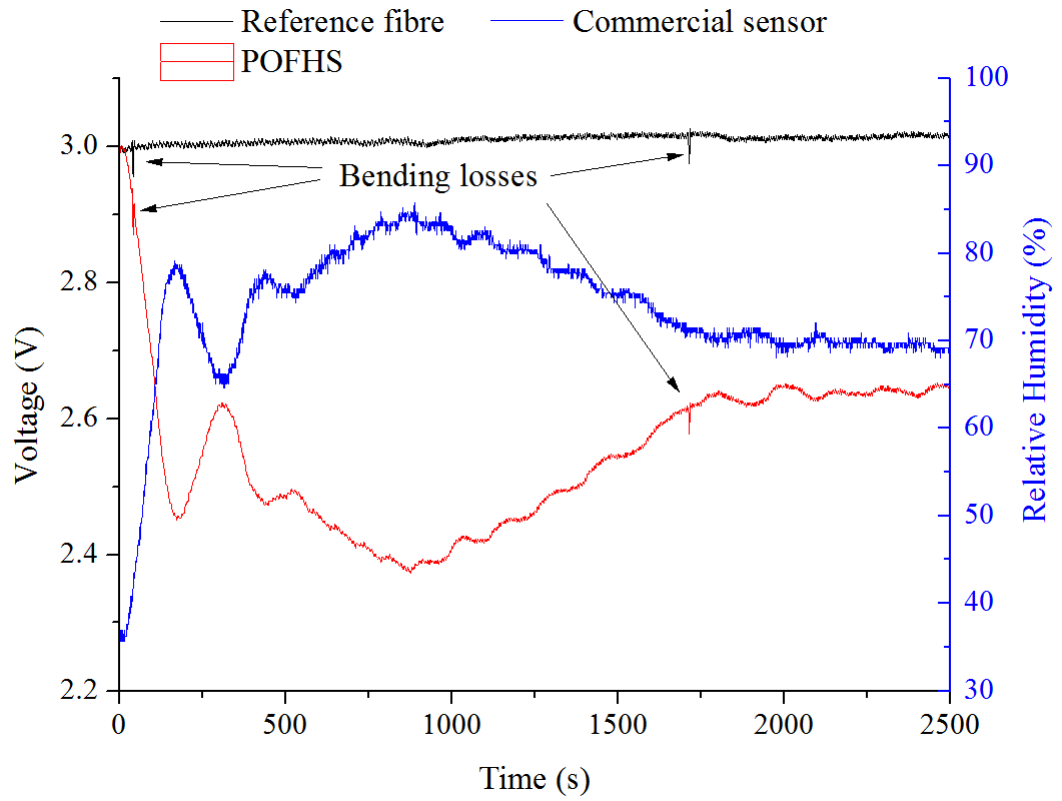


Figure 5.7: Humidity experiment with bending losses. The POFHS (red trace) and the reference fibre (black trace) were bent during a humidity experiment. Humidity measurements are compared with the commercial sensor (blue trace).

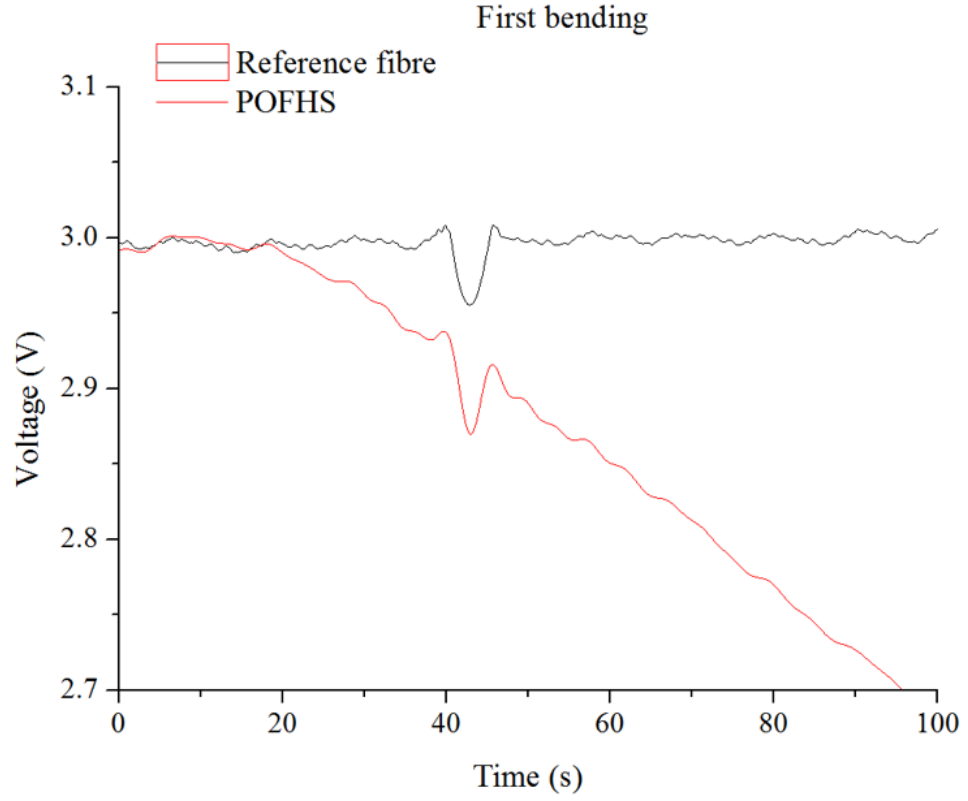


Figure 5.8: First bending loss detected on the POFHS (red trace) and the reference fibre (black trace). Zoom in from Figure 5.7.

As expected, the reference fibre registered only the bending losses whilst the POFHS recorded both the humidity changes and the bending losses. Therefore, since the reference fibre is not affected by the humidity, both signals can be subtracted in order to obtain the corresponding humidity measurements. Figure 5.9 illustrates the bending loss removal on the POFHS signal.

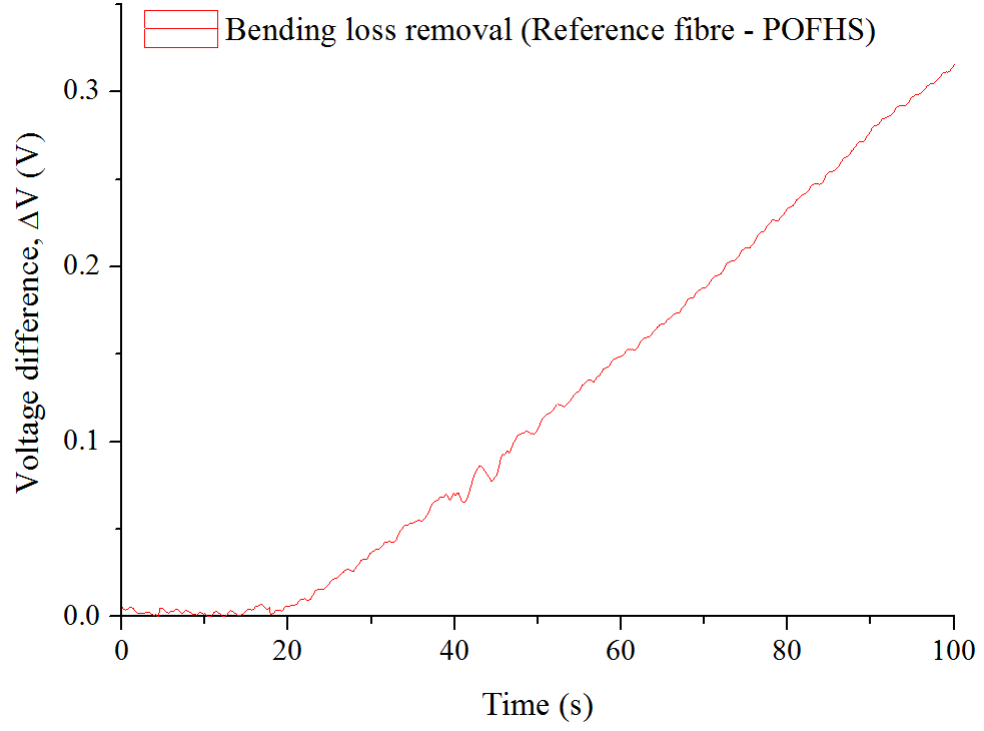


Figure 5.9: Bending loss removal from the POFHS signal.

Moreover, given the calibration curve in Figure 5.6, the POFHS signal can be expressed in RH terms. Figure 5.10 shows the POFHS response in RH terms (red trace) after removing the bending losses compared with the commercial humidity sensor (blue trace) measurements during the same experiment.

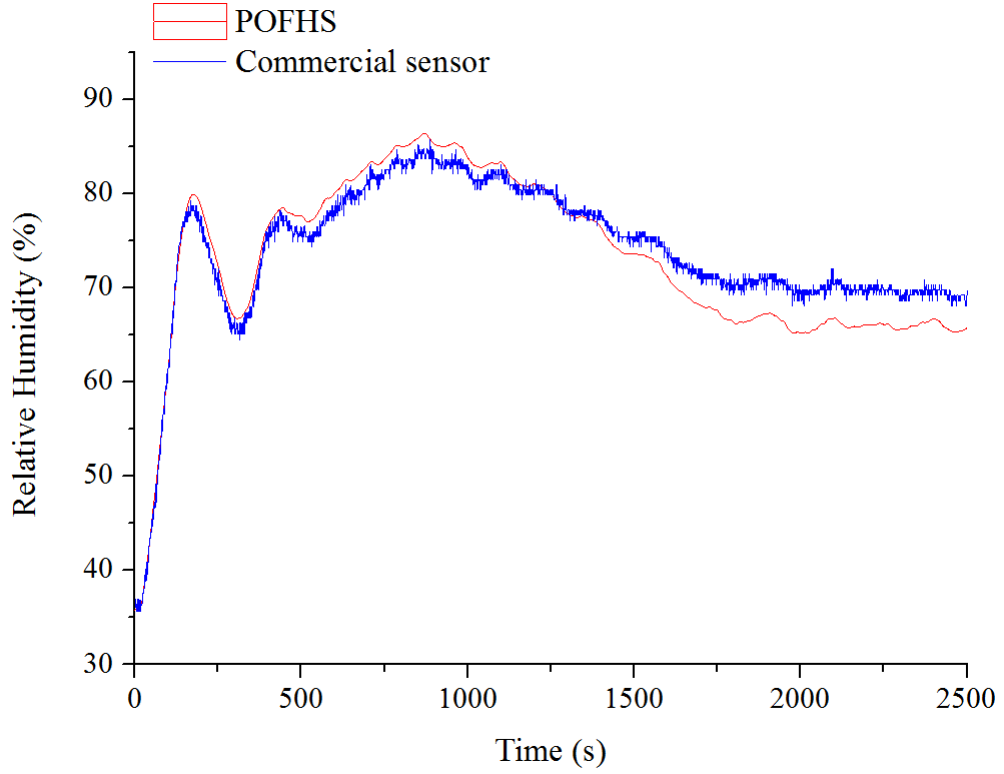


Figure 5.10: POFHS signal after removing bending losses (red trace). The calibration curve was used to convert the POFHS signal into %RH. The humidity measurements are compared with the commercial sensor response (blue trace).

The results from this test show that the reference fibre can be used to compensate perturbations on the POFHS signal due to the continuous movement or motion artefacts that can be involved in the humidity measurement on the body during exercise.

First test (POFHS on chest) for humidity measurements on body while cycling

In the first test for humidity measurements on the body while cycling the 3D-printed holder including the POFHS and the reference fibre was placed at the volunteer's chest. The commercial sensor was located next to the 3D-printed holder. Figure 5.11 shows the POFHS response compared with the commercial sensor measurements during the experiment. In this figure the bending losses registered by the reference fibre were removed from the POFHS signal to show the humidity measurements.

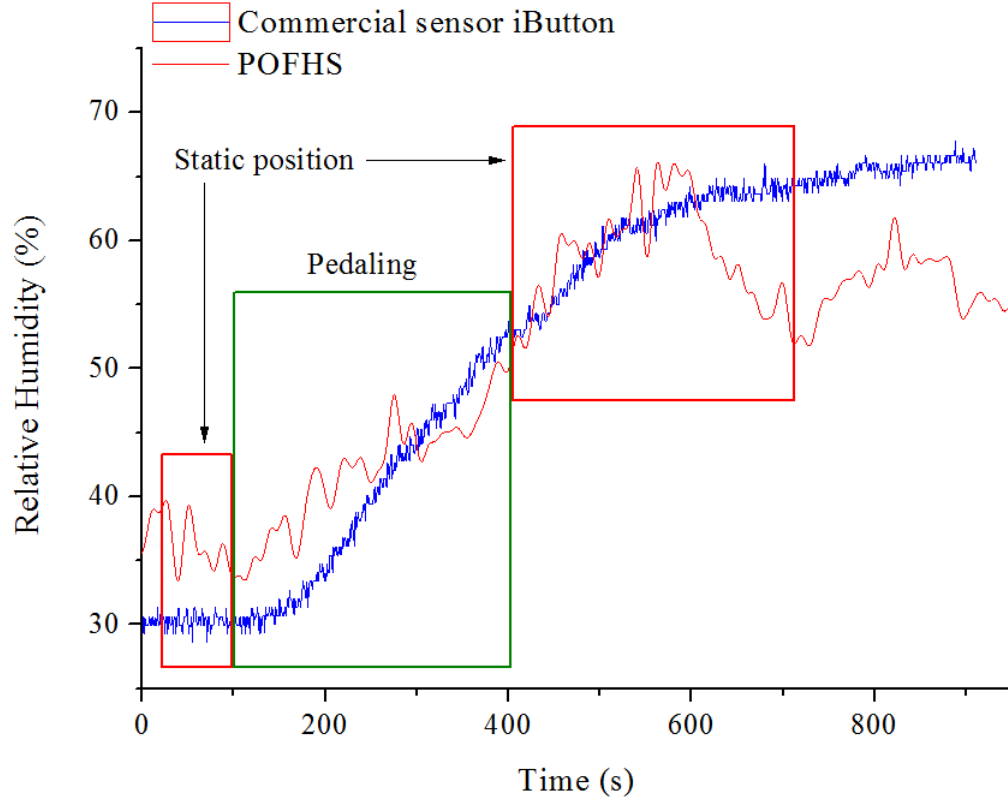


Figure 5.11: Humidity measurements at the volunteer’s chest while cycling. The POFHS measurements (after reference subtraction) are compared with the commercial humidity sensor recordings. The OFS evaluation system was used to collect the signal from the POFHS.

The POFHS and the commercial sensor recorded an increase in relative humidity while pedaling. However, a decrement in humidity is expected to be observed after pedaling due to the body relaxation and cooling down. This humidity change was recorded by the POFHS whereas the commercial humidity sensor showed a further increase in relative humidity. This effect is plausible since the commercial sensor features an aperture of 1mm diameter which entraps humidity within a chamber resulting in a slower response. In addition, the sensitive area of the commercial sensor is facing outwards to avoid saturation due to the direct contact with the skin, however, the further increase in the humidity measurements is induced due to the commercial sensor sensitive area occlusion with the volunteer’s clothing. The 3D-printed holder window prevents the POFHS to be in direct contact with the volunteer’s clothing, therefore, the decrease in humidity due to the body relaxation can be detected.

Second test (POFHS on upper back) for humidity measurements on body while cycling

The second test for humidity measurements on the body while cycling consisted of repeating twice the protocol used during the previous test, but with an extended duration. In this case, the 3D-printed holder with the POFHS and the reference fibre was placed at the volunteer's upper back. In addition, the last part of the test consisted of breathing on the POFHS in order to further increase the RH to observe the POFHS response over higher RH levels. Figure 5.12 shows the results of the second test highlighting the events described in the protocol from Table 5.6. The commercial humidity sensor was not used for this test due to the limitation noticed in the previous experiment.

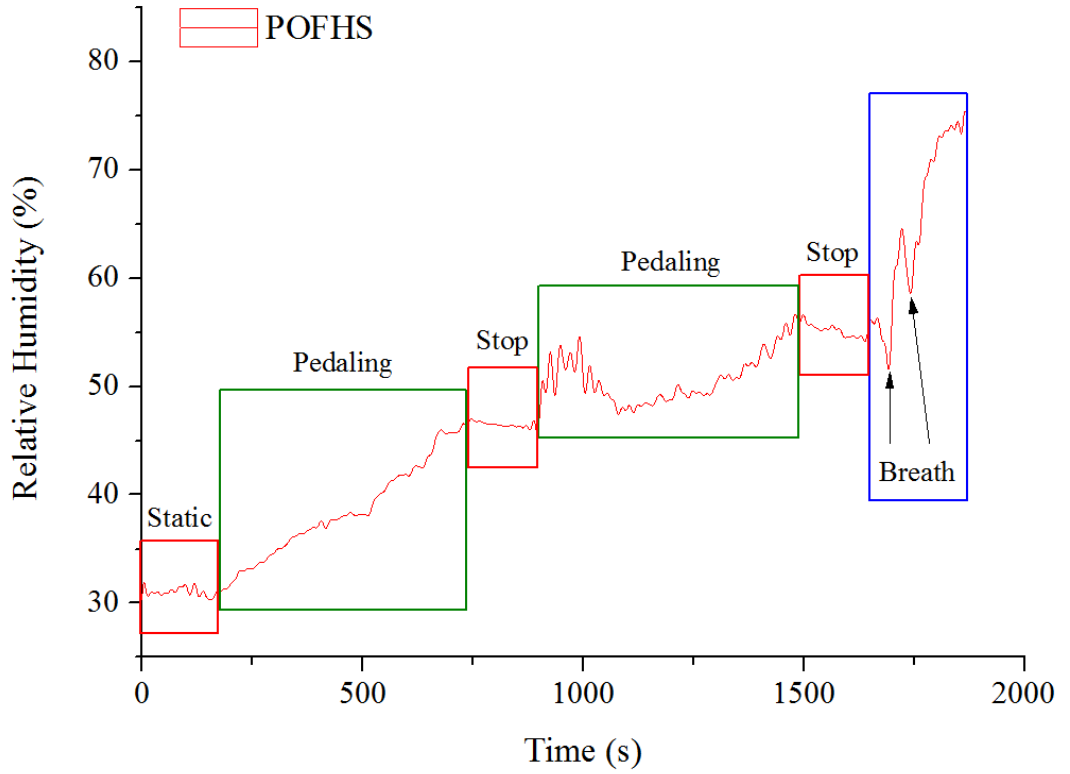


Figure 5.12: Humidity measurements at the volunteer's upper back while cycling. The OFS evaluation system was used to collect the signal from the POFHS.

It can be observed the RH increment while pedaling and the signal stabilization during static positions. During the second pedaling period an oscillation was detected in the RH due to the humidity building-up in the body after re-

pose. Moreover, after pedaling, the POFHS was exposed in order to provide two breaths on this area. A rapid decrease in the measurements was observed since the exposure of the upper back provokes a sudden humidity decrease. Furthermore, it was noticed that the POFHS responds well to breathing which increased the RH to 75% after the second breath.

5.5 Summary and comments

In this chapter, the development of a low-cost electronic portable unit to evaluate the signal from the OFSs developed in this PhD for humidity and pH measurements was described. The use of electronic components such as an LED, a photo-diode and a transimpedance amplifier replace the expensive and non-portable instrumentation used for the fabrication of the OFSs.

The OFS evaluation system has several advantages compared with the previous experimental instrumentation used namely:

1. Low-cost fabrication.
2. Small size that provides portability to the evaluation system.
3. Flexibility to be used with both the OFS for humidity and pH measurements.
4. Capability to easily replace some components such as the LED and the photo-diode if a different wavelength is required to be monitored. For example in the case of the Soret and Q bands for the OFS for pH measurements.
5. Capability to transmit the output data in real-time via wireless to a computer and to store the data in a SD card as a data back-up.

Furthermore, the portable electronic unit was used to observe the performance of

the POFHS to monitor the relative humidity expelled by the human body while cycling. The portability of the electronic circuit designed allowed the evaluation system to be located at the waist of a volunteer and to observe the test results in real-time in a computer via wireless. The initial results for the humidity measurements on the chest and the upper back from a volunteer showed promising results for the use of the POFHS in sport activities. More experiments are required to further characterize and observe the POFHS response under sport activities. Future work will include the development of a smaller holder to reduce bending losses due to movements.

In addition, the OFS evaluation system can be alternatively deployed for pH measurements. Future work will also include the test of the optical fibre pH sensor with the electronic portable unit.

The cost-effectiveness of the electronic circuit designed can be further improved by replacing some components such as the ADC and SD card modules for its main components. In addition, the alternative use of optical fibre connectors can be useful to reduce cost and size of the evaluation system.

Chapter 6

Conclusions and Future Directions

"Discovery is seeing what everybody else has seen, and thinking what nobody else has thought."

- Albert Szent-Györgyi -

6.1 Introduction

This chapter presents the conclusions from this research and a discussion about the future work with respect to potential optimization and applications of the optical fibre sensors developed and the evaluation system designed. The purpose of this chapter is also to discuss the achievement of the objectives established in the progress of this PhD (Section 1.7).

6.2 Conclusions

The implementation of fibre optic technology in healthcare and sports applications through the development of optical fibre sensors (OFS) to monitor humidity and pH was explored. In particular, applications such as wound healing monitoring, foetal blood sampling and body sweat rate during exercise were used to help define the performance requirements.

The development of optical fibre sensors for humidity and pH measurements and the design of a low-cost portable evaluation system has been explained throughout this thesis. The study of different sensing techniques and coating methods to fabricate optical fibre sensors has led to the development of a wide range non-invasive polymeric optical fibre humidity sensor (POFHS) and a narrow range OFS for pH measurements.

The fabrication of a POFHS was described. The polymeric optical fibre coated by layer-by-layer method with a hydrophilic film based on PAH/SiO₂ multilayers (7 PAH/SiO₂ layers with respect to the penetration depth of the evanescent wave) exhibited a wide operative region in the range of $\sim 10\%$ to $\sim 75\%$ RH and $90\% - 97\%$ RH with a sensitivity of -3.87×10^{-3} and -9.61×10^{-3} in transmittance percentage per RH percentage, respectively. A fast response time of 1.5s was obtained. The operation principle of this sensor is based on the interaction between the evanescent wave produced in the sensor region of the fibre and the sensitive film with respect to the surrounding relative humidity.

The incorporation of the POFHS within wound dressings provided encouraging

results to create a wound dressing that can remotely monitor the wound status. This can help to tackle the problem of unnecessary removal of the dressing that will result in discomfort in patients and potential disruption of wound healing. Moreover, preliminary experiments to monitor the humidity expelled from the body during cycling were performed providing a sensitivity of 13mV/%RH recorded with the OFS evaluation system designed. These results open up the feasibility of the implementation of this sensor into sportswear to monitor the body response under exercise. Combining the POFHS and the OFS for pH measurements has the potential to lead to improvement of exercise routines and nutrition via sweat analysis.

In the case of the OFS for pH measurements, the optical fibre was bent into a U-shape to further increase the evanescent wave penetration depth. The sensitive region was coated with a sol-gel film which included a dye compound (TSPP) as a pH indicator. The principle of operation consisted of the evaluation of the light absorption produced in two wavelength regions (Soret and Q absorbance bands) over a range of pH values. Over the pH range of 6.72 - 8.16 there was a sensitivity of 0.032 and -0.054 in absorbance units per pH units for the Soret and the Q band, respectively. The response time observed was 42s.

Moreover, the use of the OFS for pH measurements has the potential to be exploited to obtain more information in-situ about the pH in foetal blood sampling during newborn delivery. Results obtained with the pH sensor provided a novel approach to obtain measurements within a narrow range which can be helpful to counteract the limitations of the current techniques and devices used, for example, blood sampling collection with capillary tubes. Limitations of this technique such as insufficient blood collection, air trapped within the capillary tube or blood clotting require additional samples to be taken. The implementation of the optical fibre pH sensor during the scalp incision can yield more information in real-time to take an early decision for intervention in newborn delivery which can be of impact to reduce risk of damage to newborn health. In addition the non-toxicity of the pH indicator can be of benefit for the implementation of the OFS for pH measurements for monitoring the pH of the wound exudate.

The response of both sensors can be obtained with the evaluation system designed. The manufacturing of a low-cost small portable electronic unit was useful for the remote assessment of the humidity changes on the body during cycling. Moreover, the electronic unit can be of benefit to observe the pH measurements in real-time without disturbing the space in the delivery room during foetal blood sampling since measurements can be remotely observed.

In conclusion the potential of optical fibre sensors for healthcare and sports applications has been initially demonstrated but there is still further work to be conducted in order to realise this potential.

6.3 Future directions

The work presented in this PhD thesis provided promising results from the development of optical fibre sensors for humidity and pH measurements for healthcare and sports applications. In addition, the design of an evaluation system produced a portable electronic unit that can be used to observe the sensor response via wireless in real-time. In this section, the future work and studies proposed for the further optimization of the sensors developed are described.

6.3.1 Polymeric optical fibre humidity sensor

There exist a series of characteristics to be further studied from the fabrication of the POFHS. For example, additional studies are suggested to determine the sensitive film lifetime and leachability under humid environments such as the effect of sweat in contact with the sensitive film since the pH from sweat can be disruptive for the film structure.

Moreover, in Section 3.6.3 the cross-sensitivity of the POFHS with temperature was observed. However, further studies will be produced to observe the cross-sensitivity of the POFHS over higher temperatures which can affect the self-consistency of the film.

The POFHS also provided pilot data for the integration in textiles. Future work will involve the integration of the POFHS within different garments to observe the sensor performance. The commercial technology to embed the sensor within textiles will be provided by for example a collaboration with the company Footfalls & Heartbeats Ltd. Examples of the potential techniques for the embedding of the POFHS within textiles are presented in [145, 146]. The weaving technique is suggested for the integration of the POFHS within textiles. This is a low-bending process that allows the exposure of the POFHS sensing region, as shown in Figure 6.1.

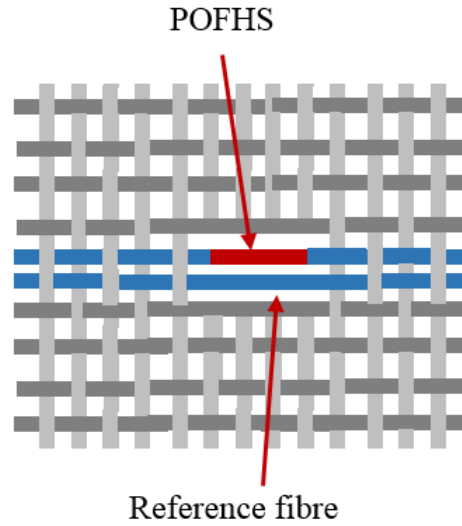


Figure 6.1: Suggested technique for the integration of the POFHS and the reference fibre within textiles.

In addition, to further this research, there is the intention to obtain ethical approval to measure humidity on the wound surface using the POFHS embedded within a dressing. Additional studies will be required to observe the interaction between the sensor and the plausible contact with the wound exudate. This needs also to be considered in terms of the Biocompatibility standard ISO 10993 (an important requirement of any medical device in contact with the human body).

In Section 5.4.3 the POFHS performance to monitor humidity from the body during cycling was tested. Additional experiments with more volunteers on sport activities will help to further characterise the POFHS response in order to monitor

the sweat rate which can provide information to observe the athlete's dehydration level. For example, the POFHS can be used during activities such as running on a treadmill or during competitions since measurements can be obtained remotely in real-time. In addition, the POFHS is capable of being worn with sportswear without compromising the athlete's performance or the competition fairness with other athletes. Moreover, as described in Section 1.4 the body has regions where more sweat is produced [63, 64]. Taking into consideration these regions, integration of the POFHS within headbands and sport shirts can be beneficial. These studies would be possible through a collaboration with a company leader in the innovation and development of sportswear.

In addition, as explained in Section 5.4.2, the POFHS was inserted in a 3D-printed holder to reduce bending losses. Further work will include the design of a small tubular holder to further reduce bending losses.

6.3.2 Optical fibre pH sensor

In the case of the optical fibre pH sensor, as part of the motivation presented in Section 1.8, one of the potential uses for this sensor is in medical applications, for example to monitor the pH in foetal blood sampling. Moreover, in Section 2.1 the limitations and complications of the current techniques used for foetal blood sampling procedure are explained. The application of the evaluation system designed in conjunction with the OFS pH sensor can be useful to provide pH measurements in-situ, reducing time normally spent while taking the sample to the laboratory for analysis.

The small size of the optical fibre pH sensor can be used as an alternative for the use of capillary tubes for the collection of blood samples from the foetal scalp, as illustrated in Figure 6.2. Moreover, in Section 4.3, it was discussed the properties of the pH indicator used for the development of the OFS for pH measurements. TSPP has been used for in-vivo applications such as DNA concentration measurements or during photodynamic therapy for tumour location due to its non-toxicity [207, 210]. Therefore, the OFS for pH measurements can be suitable for the use in foetal blood sampling technique to obtain pH measurements in-situ.

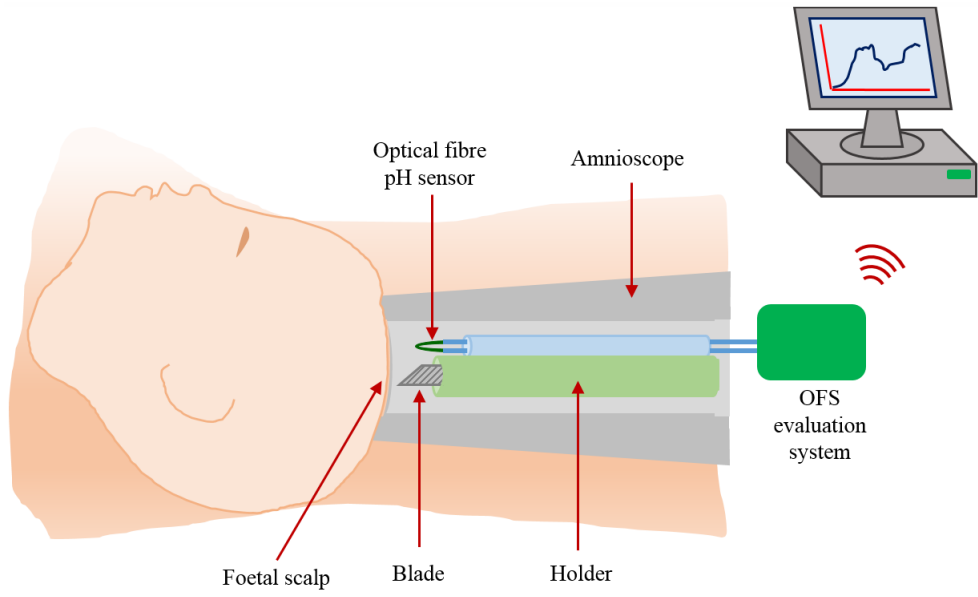


Figure 6.2: Proposed application of the OFS for pH measurements for foetal blood sampling (FBS).

Unfortunately, due to the amount of time left in the process of the PhD the pH test with both the portable OFS evaluation system and the pH sensor was not carried out. However, as a future work, Figure 6.3 illustrates the proposed set-up for operation of the OFS evaluation system with the pH sensor developed.

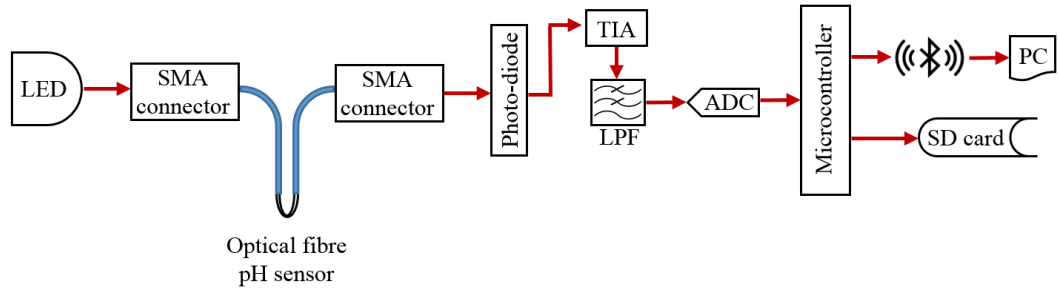


Figure 6.3: Proposed set-up for pH measurements with the OFS evaluation system and the OFS pH sensor developed.

Conversely to the set-up for humidity measurements (Figure 5.4), the reference with respect to the bending losses was not included since measurements are obtained from the insertion of the probe into the sample solution. Therefore, motion artefacts are not expected during measurements, provided the sensor is appropriately fixed. However, the evaluation system can be re-designed to include

several sensors to obtain multiple measurements either from the same or different samples. In addition, future work will include the manufacture of a holder for the sensor since the geometrical configuration (U-shape) can be confined within a tubular holder in order to avoid external perturbation such as bending losses. Moreover, further studies will be undertaken to observe the limitations of the sensor over a wider pH range and the temperature effect on the sensitive film by monitoring different wavelengths of the spectrum.

6.3.3 Evaluation system

The electronic unit designed supplied the requirement of a portable unit for remote measurements. In this case, the future work will concentrate on the minimization of the size of the electronic unit. In order to reduce the size and thickness of the electronic unit, some components such as the SD card and the ADC modules can be replaced by a SD card socket and the IC for the ADC conversion, respectively.

The PCB has the capability to replace certain components such as the LED and the photo-diode if a different wavelength is required to monitor or if any of these components are damaged. For example, the OFS for pH measurements requires the monitoring of the Soret and Q absorption bands. The LED and the photo-diode can be replaced by components with high luminous intensity and high sensitivity over these wavelength regions.

Moreover, future work will include the re-design of the PCB in order to manufacture the electronic circuit in a flexible PCB which can be beneficial to increase wearability and the user's comfort. The future work also consists of the investigation about the use of different fibre connectors such as the lucent connector (LC) or plastic optical fibre connectors in order to replace the SMA bulkhead receptacles required to fix the LED and the photo-diode and the SMA optical connectors used for the OFS alignment, hence reducing cost and size.

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Appendix A

Microcontroller code

```

#include <stdint.h>
#include <Wire.h>
#include <Adafruit_ADS1015.h>

Adafruit_ADS1115 ads(0x48);

float REF = 0.0;
float POFHS = 0.0;
float RH;
float i=0;
double a;

void setup()
{
  Serial.begin(115200);
  ads.begin();
  Serial.println("Time   REF DOWN  OFS UP  RH");
  Serial.println("ms     V      V    %");
  Serial.println();
  Serial.println();
  Serial.println();
}

void loop()
{
  int16_t adc0;
  int16_t adc1;

  adc0 = ads.readADC_SingleEnded(0);
  adc1 = ads.readADC_SingleEnded(1);

  REF = (adc0 * 0.1875)/1000;
  POFHS = (adc1 * 0.1875)/1000;

  RH = ( (REF - POFHS) / 0.013 ) + 3.76;

  a = i/10;

  Serial.print(a);
  Serial.print(" ");
  Serial.print(REF,3);
  Serial.print(" ");
  Serial.print(POFHS,3);
  Serial.print(" ");
  Serial.print(RH,3);
  Serial.println();
  i++;
  delay(100);
}

```

Figure A.1: Microcontroller C code for data conversion of the POFHS signal into %RH terms.

Appendix B

Electronic circuit schematic diagram

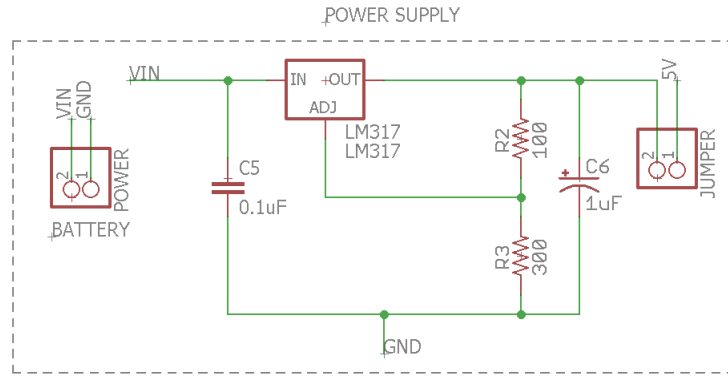


Figure B.1: Power supply section.

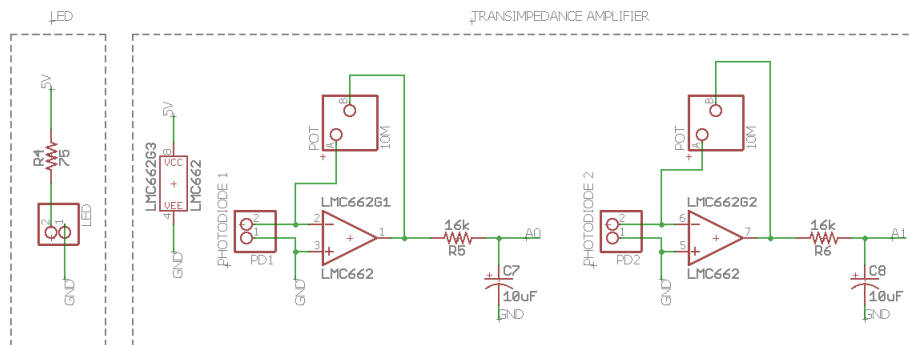


Figure B.2: Transimpedance amplifier section.

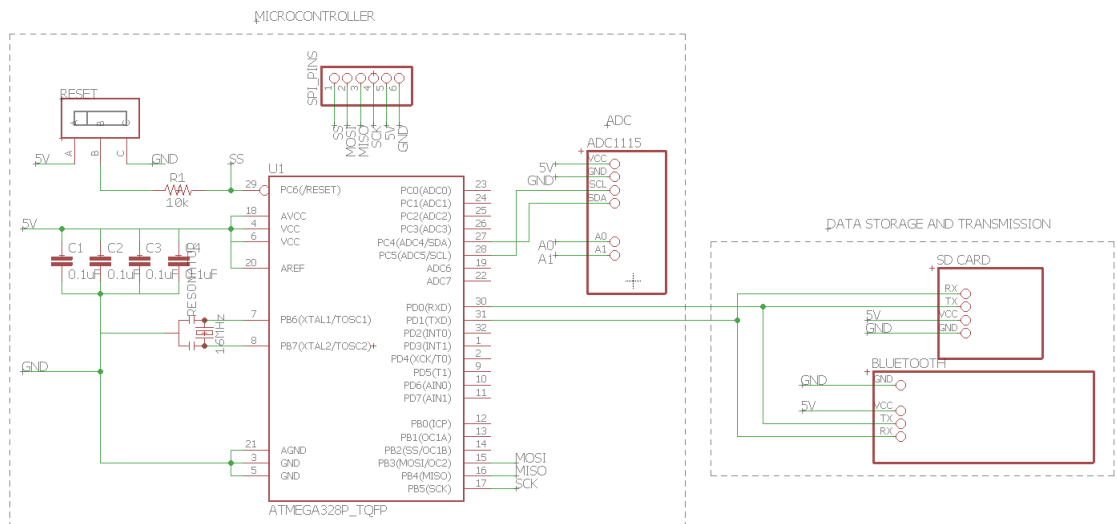


Figure B.3: Microcontroller and data transmission section.

Appendix C

PCB layout

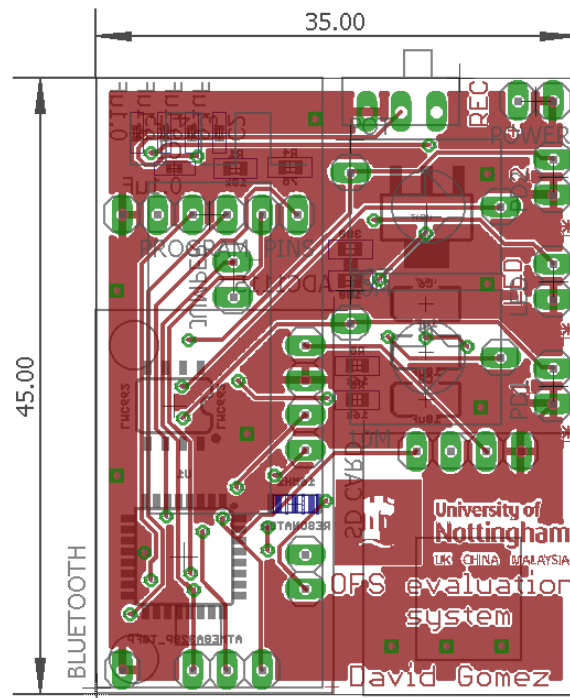


Figure C.1: Printed circuit board, top view.

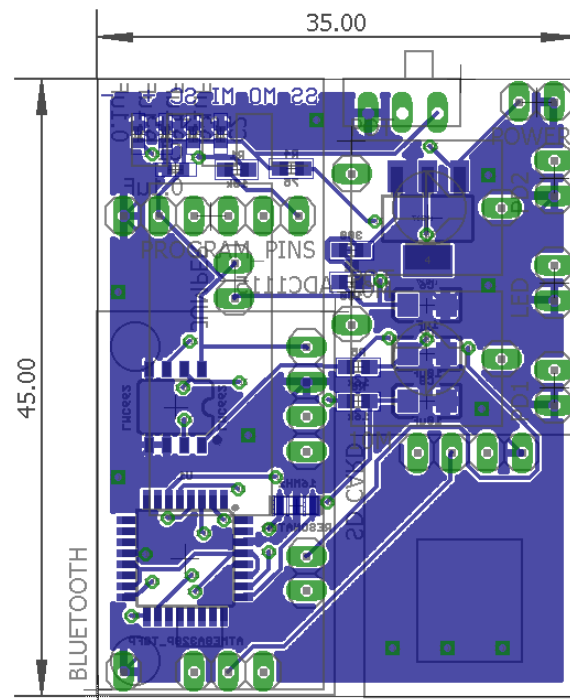


Figure C.2: Printed circuit board, bottom view.

Appendix D

Experiment ethics approval

Experimental study to demonstrate humidity detection on skin with a Fibre Optic Sensor

Participant Information Sheet

Experimenter: David Gomez

david.gomez@nottingham.ac.uk

Supervisor: Prof. Stephen P. Morgan

Steve.morgan@nottingham.ac.uk

You are invited to take part in a study which will investigate whether humidity on skin surface can be detected by a fibre optic sensor. Before you decide whether to take part it is important for you to understand why the research is being done and what it will involve. For any queries or information please contact david.gomez@nottingham.ac.uk

Background

The common techniques for monitoring wounds either compromise the process of healing or have low accuracy to detect the status of a wound. One of these techniques consists in removing wound dressing to verify the wound state; this tends to compromise wound healing. Novel optical sensing technology [1], developed in the Applied Optics Group at the University of Nottingham can be used to detect the correct healing of a wound using Fibre Optic Sensors. The objective of the PhD project is to investigate whether this sensing technology can be incorporated into textile to obtain better diagnosis for wound healing.

One of the parameters that require special care during the stages of wound healing is moisture level due to the facility of cell proliferation and migration within a moist environment [2] [3]. For this reason, the study will focus in the detection of humidity on skin surface in order to monitor the sensitivity of a Fibre Optic Sensor coated with a hydrophilic film (PAH/SiO₂ nanoparticles).

Further work will be related to the detection of markers involved in wound healing such as wound exudate pH, wound moisture and proteases levels in wounds [4]. This will lead into an inexpensive sensing technology that can be integrated within textiles to improve diagnosis and, therefore, more accurate wound management decisions.

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Who are the participants?

10 healthy volunteers will be recruited from the Applied Optics group including researchers/PhD students. Volunteers should not smoke and avoid drinking caffeine 3 hours before the study takes place.

Procedure

Measurements will be performed under standardized conditions (room temperature of 21 °C to 23 °C and a humidity level of 45% to 55%). Before the study, you will be asked to clean your hands using an alcohol-free foam hand sanitizer provided by the experimenter and wait for 5 minutes to allow your hands to acclimatize to the environment.

In the study, a standard digital camera will be used to take a photograph of your hands. You will be asked to put your right hand still on the setup for 5 minutes. After this, you will need to remove your hand from the setup. Then, you will be asked to clean again your hands using the sanitizer and leave them with your palms up for 5 minutes. This process will be repeated 5 times.

The setup as shown in Fig. 1 consists in a petri dish containing a commercial humidity sensor (iButton Hygrochron Temperature/Humidity Logger DS1923) and a Fibre Optic Sensor developed within the Applied Optics Group. In addition to this, during the study, humidity will be recorded by One-Wire-Viewer and Spectra-Suite software for the humidity sensor and

the Fibre Optic Sensor, respectively. These results will be compared with a reference Fibre Optic Sensor. The study should last approximately 45 minutes for each participant.

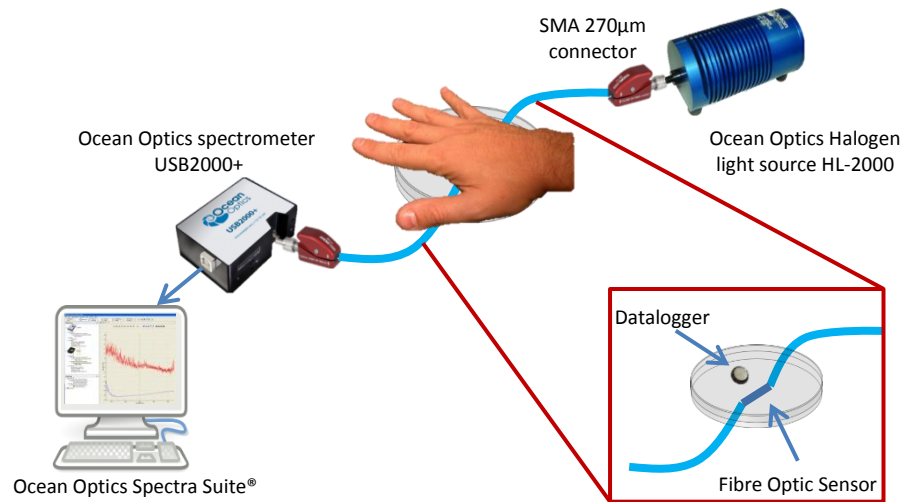


Figure 1. Setup for humidity detection on skin surface with Fibre Optic Sensor study

The second part of the study involves attaching the Fibre Optic Sensor to a bandage and wrapping it around the forearm. The humidity will be monitored for a period of approximately 15-20 minutes until the humidity values reach a constant value.

It is important to mention that the volunteer will not feel any discomfort with any of the parts of the study since no adhesives will be used on the skin and the bandage will not be wrapped tightly.



Figure 2. Measurements of humidity on forearm [4]

Part 2: Further Information

1. Do I have to take part?

No. Participation in the study is entirely voluntary; it is up to you to decide whether or not to take part. If you do decide to take part you will be given this Participation Information Sheet to keep and be asked to complete a consent form. However, even if you complete the consent form you are still free to withdraw at any time and without giving a reason.

2. What will happen to me if I take part?

You will be asked to read through the Participant Information Sheet and then asked to complete the Participant Consent Form.

3. What will happen if I do not want to carry on with the study?

You can withdraw from the study at any time without having to provide a reason. If you do withdraw information that can be attributed to you will not be used in the analysis.

4. Will I be paid?

For this study, there will not be compensation for your participation.

5. Will my taking part in this study be kept confidential?

Yes. All information which is collected about you during the course of the research will be kept strictly confidential and our procedures for handling, processing, storage and destruction of your data are compliant with the Data Protection Act 1998. The information will be retained for 7 years following any publication, after this time it will be destroyed. All of the data will be stored on password protected computers in the research laboratory of the Applied Optics Group. Only members of the research group will have access to the data. It will not be possible to identify any individuals because all data will be published anonymously.

6. What will happen to the results of the research study?

The results will be used to determine the feasibility of the usage of Fibre Optic Sensors within textiles to detect correct wound healing. Besides, the collected data will be used in conferences and journal publications. In addition to this, all information will be published anonymously and it will be kept strictly confidential. If you have any distinguishing features in your photographs that might be used to identify you (e.g. a tattoo) then these will be obscured if published.

7. Who has reviewed the study?

The study has been approved by the University of Nottingham, Faculty of Engineering Ethical Review Committee.

Consent form

Experimental study to demonstrate humidity detection on skin with a Fibre Optic Sensor

- I confirm that I have read the information sheet and have had the opportunity to ask questions.
- I understand that the collected data will be used for journal publications.
- I understand that I am free to withdraw at any time and that the any information will be destroyed and not used.
- I understand that all information collected during the study will be kept strictly confidential.
- I agree to take part in the above study.

☐☐☐☐☐

Name

Signature

Date

Participant information:

Study Case Number:

Age:

Gender:

☐ M

☐ F

Have you had any recent wound in the hands?

Yes

☐

No

☐

If yes, please describe the cause of the injury and how long ago it happened:

Ethics Committee Reviewer Decision

This form must be completed by each reviewer. Each application will be reviewed by two members of the ethics committee. Reviews may be completed electronically and sent to the Faculty ethics administrator (Jo Deeley) from a University of Nottingham email address, or may be completed in paper form and delivered to the Faculty of Engineering Research Office.

Applicant full name: David Gomez

Reviewed by:

Name Gary Burnett

Signature (paper based only)

Date 21/08/2015.....

- ☒ Approval awarded - no changes required
- ☐ Approval awarded - subject to required changes (see comments below)
- ☐ Approval pending - further information & resubmission required (see comments)
- ☐ Approval declined – reasons given below

Comments:

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Please note:

1. The approval only covers the participants and trials specified on the form and further approval must be requested for any repetition or extension to the investigation.
2. The approval covers the ethical requirements for the techniques and procedures described in the protocol but does not replace a safety or risk assessment.
3. Approval is not intended to convey any judgement on the quality of the research, experimental design or techniques.
4. Normally, all queries raised by reviewers should be addressed. In the case of conflicting or incomplete views, the ethics committee chair will review the comments and relay these to the applicant via email. All email correspondence related to the application must be copied to the Faculty research ethics administrator.

**Any problems which arise during the course of the investigation must be reported to the
Faculty Research Ethics Committee**

Experimental study to demonstrate humidity detection on the skin during exercise with a fibre optic sensor embedded into a textile

Participant Information Sheet

Experimenter: Lucy Elmer
lucy.elmer@nottingham.ac.uk

Experimenter: David Gomez
david.gomez@nottingham.ac.uk

Supervisor: Dr. Sergiy Korposh
s.korposh@nottingham.ac.uk

You are invited to take part in a study which will investigate whether changes in humidity on the skin surface can be detected during exercise by a fibre optic sensor embedded into a textile. Before you decide whether to take part it is important for you to understand why the research is being done and what it will involve. For any queries or information please contact lucy.elmer@nottingham.ac.uk

Background

It is important to monitor humidity levels during exercise to ensure safe human thermoregulation can occur. The body excretes sweat during physical activity as a cooling mechanism when its core temperature increases. [1] In dry environments sweat evaporates leaving a cool layer of air on the skin and so reducing the body's core temperature. However, in humid conditions water molecules in the air are more concentrated, consequently the water molecule concentration gradient between the sweat and the air is reduced. [1] Sweat evaporates at a slower rate which can result in the body's temperature continuing to increase as it is unable to dissipate the heat it is producing. This is dangerous as it leads to an increased risk in hyperthermia and dehydration.

Conversely in less humid environments the body inhales the drier air and absorbs the moisture present in the lungs and respiratory tract. This reduces the performance of the lubricated layer which can make breathing uncomfortable. This is problematic in sports applications as it can reduce performance during exercise. [1]

Technology developed in the Optics and Photonics at the University of Nottingham has produce an optical fibre which when coated with a hydrophilic film (PAH/SiO₂ nanoparticles) can detect changes in the environment's humidity level. [2] The experiment will focus on the detection of humidity on surface of the skin during exercise. It will be monitoring the response of a fibre optic sensor modified with the humidity sensitive layer and embedded into a wearable textile. This will be an extension of the previous work by David Gomez. Subsequently the 'Important Questions' section of this ethical approval request will be the same as his previously approved applications. [3]

Procedure

The experiment will be undertaken under standardized conditions: room temperature of 21 °C - 23 °C and humidity level of 45% - 55%. During the study a digital phone camera will be used to photograph the areas being measured: chest and back as highlighted in Figure 1: Heat map of workout sweat spots [4].

Before the study, you will be asked to complete a short survey to confirm your suitability as a participant. The study will take approximately 60 minutes in total. The following procedure will occur twice, first measuring humidity at the chest area and then at the back area:

1. You will be asked to clean the measured area using an alcohol-free foam hand sanitizer provided by the experimenter and wait for 2 minutes to allow this skin area to acclimatize to the environment.
2. The fibre optic sensor embedded into a holder or a textile will be attached to the measured area using micropore tape, as will the commercial sensor. The humidity will be measured throughout the experiment using both sensors.
3. You will be asked to confirm that the sensors are comfortable and you are ok to proceed with the experiment.
4. You will then climb stairs on a Stairmaster machine for 3 minutes.
5. You will then rest for 3 minutes.
6. Steps 1-5 will be repeated 3 times

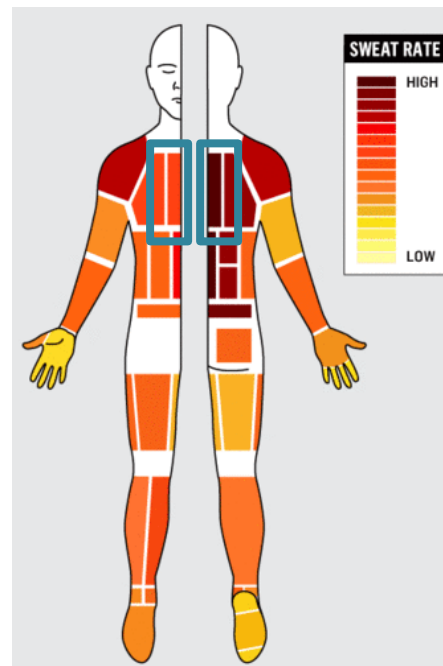


Figure 1. Heat map of workout sweat spots [4]

References

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- [2] D. Gomez, S. M. Morgan, B. R. Hayes-Gill, R. Goncalves Correia and S. Korposh, "Polymeric optical fibre sensor coated by SiO₂ nanoparticles for humidity sensing in the skin microenvironment," *Elsevier*, vol. Sensors and Actuators B, no. 254, pp. 887-895, 27 07 2017.
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Part 2: Further Information

1. Do I have to take part?

No. Participation in the study is entirely voluntary; it is up to you to decide whether or not to take part. If you do decide to take part, you will be given this Participation Information Sheet to keep and be asked to complete a Participation Questionnaire and a Participant Consent Form. However, even if you complete the consent form you are still free to withdraw at any time and without giving a reason.

2. What will happen to me if I take part?

You will be asked to read through the Participant Information Sheet and then asked to complete a Participation Questionnaire and a Participant Consent Form.

3. What will happen if I do not want to carry on with the study?

You can withdraw from the study at any time without having to provide a reason. If you do withdraw information that can be attributed to you will not be used in the analysis.

4. Will I be paid?

For this study, there will not be compensation for your participation.

5. Will my taking part in this study be kept confidential?

Yes. All information which is collected about you during the course of the research will be kept strictly confidential and our procedures for handling, processing, storage and destruction of your data are compliant with the Data Protection Act 1998. The information will be retained for 7 years following any publication, after this time it will be destroyed. All of the data will be stored on password protected computers in the research laboratory of the Optics and Photonics Group. Only members of the research group will have access to the data. It will not be possible to identify any individuals because all data will be published anonymously.

6. What will happen to the results of the research study?

The results will be used to determine the feasibility of the usage of Fibre Optic Sensors within textiles to detect humidity levels in sports applications. Besides, the collected data will be used in conferences and journal publications. In addition to this, all information will be published anonymously and it will be kept strictly confidential. If you have any distinguishing features in your photographs that might be used to identify you (e.g. a tattoo) then these will be obscured if published.

7. Who has reviewed the study?

The study has been approved by the University of Nottingham, Faculty of Engineering Ethical Review Committee.

Participant Questionnaire

Experimental study to demonstrate humidity detection on the skin during exercise with a fibre optic sensor embedded into textile

Please read the following questions carefully and answer the following questions honestly and to the best of your knowledge.

Question	Answer (Delete as appropriate)
Are you male or female?	Male / Female
Are you aged between 18-25?	Yes / No
Do you smoke?	Yes / No
Have you consumed alcohol or drugs in the past 6 hours? This includes performance enhancement drugs and any prescription medication.	Yes / No
Have you consumed caffeine in the past 6 hours? This includes caffeine pills/ tea/ coffee/ soft drinks.	Yes / No
Have you had any recent colds or illnesses which could inhibit your performance during exercise?	Yes / No If 'Yes' please give details:
Do you have any underlying conditions which could inhibit your performance during exercise for example: pregnancy, high blood pressure, heart problems, asthma?	Yes / No
Have you had any recent wounds to the measured areas?	Yes / No If 'Yes' please give details of the injury and how long ago it occurred:

Volunteer Number

Participant consent form

Experimental study to demonstrate humidity detection on the skin during exercise with a fibre optic sensor embedded into textile

- ☐ I confirm that I have read the information sheet and have had the opportunity to ask questions.
- ☐ I confirm that I have read and completed the participant questionnaire honestly and to the best of my knowledge.
- ☐ I understand that the collected data will be used for journal publications.
- ☐ I understand that I am free to withdraw at any time and any information will be destroyed and not used.
- ☐ I understand that all information collected during the study will be kept strictly confidential.
- ☐ I agree to take part in the above study.

Name

Signature

Date

Ethics Committee Reviewer Decision

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Applicant full name: Lucy Elmer

Reviewed by:

Name D07

Signature (paper based only)

Date 05/12/2017.....

- ☒ Approval awarded - no changes required
- ☐ Approval awarded - subject to required changes (see comments below)
- ☐ Approval pending - further information & resubmission required (see comments)
- ☐ Approval declined – reasons given below

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