Optical Fibre Sensor for fuel cell and other fluid concentration measurement

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Declaration

This thesis is written to meet the requirements for the degree of Doctorate of Philosophy. It is entirely my own work and has not been submitted to any other university or higher institution. Where the work of other people has been used, it has been fully referenced and acknowledged.

Signed:

Matthias Fabian
This work describes the development of a fibre-optic fluid concentration sensor that is based on evanescent field absorption. In addition, a second optical sensor principle is investigated by means of the development of a novel type of low insertion loss fibre-cavity.

The absorption sensor probe is evaluated on several widely applied liquid mixtures, i.e., the aqueous solutions of acetone, ethanol, methanol, 1-propanol and 2-propanol. The need to efficiently monitor these fluids emerges from the ever increasing research activity in liquid feed fuel cells which operate on, amongst others, the four latter alcohol/water mixtures. A comprehensive investigation of the influence of different fibre parameters and geometries (e.g. fibre core radius, numerical aperture and bend radius) on the sensitivity of various sensor probes is carried out theoretically as well as experimentally. Broadband measurements in the visible wavelength area are carried out in order to select the most suitable wavelength for further experiments with a low cost LED-based hardware setup. It will be shown that the novel meander-shaped sensor probe exceeds the sensitivity of a standard U-bend sensor almost 20-fold.

Fibre-cavities offer the possibility to operate absorption based optical fibre sensors in a particular configuration, the so called ringdown scheme. Current approaches suffer from high insertion loss and costly as well as stationary equipment. The cavity proposed in this investigation shows how those drawbacks can be overcome. It is treated separately in order to estimate the gain in sensitivity it can provide, independent of the type of sensor that is inserted into the cavity. The novel design reduces the insertion loss of common passive fibre-cavity designs, i.e. close to 100%, to normal fibre coupling loss.

The aim of this work is to provide a fundamental investigation into a highly sensitive refractive index sensor solution that is applicable to a wide range of liquid mixtures rather than being specifically designed for a single purpose. The application range could be further extended to areas where existing sensors are based on the same elementary optical sensor principle such as pH monitoring.

It will be shown that the proposed sensor solution combines high sensitivity with small sensor dimensions, a fast response time, low production and operational cost
and ease of operation. Hence, both approaches the evanescent field absorption sensor as well as the fibre-cavity design show significant improvement over currently applied techniques.
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I wish to thank the Irish Research Council for Science, Engineering and Technology for funding this work.

Finally, I would like to thank my family and friends.
Glossary of symbols and abbreviations

\( \alpha \)  
Absorption coefficient

\( \bar{\nu} \)  
Wavenumber

\( \delta n \)  
Refractive index difference

\( \delta n/\delta T \)  
Temperature coefficient

\( \delta n/\delta \lambda \)  
Chromatic dispersion (wavelength dispersion)

\( \delta V \)  
Voltage difference

\( \delta \)  
Lower integration limit for \( \delta \)

\( \delta \)  
Transformed angle of incidence at the inner surface of a bent planar optical waveguide

\( \delta \)  
Upper integration limit for \( \delta \)

\( \epsilon \)  
Permittivity, molar absorptivity or extinction coefficient of a medium

\( \epsilon_0 \)  
Permittivity of vacuum

\( \eta \)  
Viscosity of a medium

\( \gamma \)  
Evanescent absorption coefficient

\( \gamma_{\text{eff}} \)  
Effective evanescent absorption coefficient

\( \lambda \)  
Wavelength, decay rate

\( \nu \)  
Frequency

\( \omega \)  
Angular frequency
\( \phi \) Transformed angle of incidence at the outer interface of a bent planar optical waveguide

\( \phi_1 \) Lower integration limit for \( \phi \)

\( \phi_2 \) Upper integration limit for \( \phi \)

\( \rho \) Density, fibre core radius, radius

\( \tau \) Decay time constant of an optical signal trapped in an optical cavity

\( \Phi_0 \) General angle of incidence

\( \Phi_i \) General angle of refraction

\( \Phi_c \) Critical angle (total internal reflection)

\( \Phi_i \) Incident angle of a ray of light with the axis of an optical waveguide

\( \Phi_z \) Incident angle of a ray of light at the core/cladding interface of an optical waveguide

\( \Phi_{i(max)} \) Maximum value for \( \Phi_i \) for a given optical waveguide

\( \Phi_{z(min)} \) Minimum value for \( \Phi_z \) for a given configuration

\( A \) Absorption, Amplitude

\( B \) Offset

\( c \) Speed of light in a medium, concentration of a medium in a mixture

\( c_0 \) Speed of light in vacuum

\( d + p \) Penetration depth of the evanescent field surrounding an optical waveguide into an absorbing medium

\( E \) Electric field component of an electromagnetic wave

\( E_0 \) Overall cell voltage (of a fuel cell)

\( E_{sp} \) Specific energy of a substance

\( I \) Intensity of light, electrical current

\( I_0 \) Amplitude of the intensity of light

\( I_n \) Intensity of an optical pulse after \( n \) round trips in an optical cavity
<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>$I_{ph}$</td>
<td>Electrical current through a photodiode</td>
</tr>
<tr>
<td>$k$</td>
<td>Dielectric constant of a medium (relative permittivity), general factor</td>
</tr>
<tr>
<td>$l$</td>
<td>Path length (in the context of the absorption of light), distance</td>
</tr>
<tr>
<td>$L_p$</td>
<td>Distance between two consecutive reflections of a ray of light along a fibre core</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Molecular weight of a substance</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of ray reflections per unit length</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons, refractive index, number of round trips of a light pulse in an optical cavity</td>
</tr>
<tr>
<td>$n_0$</td>
<td>Refractive index of air</td>
</tr>
<tr>
<td>$n_1$</td>
<td>Core refractive index</td>
</tr>
<tr>
<td>$n_2$</td>
<td>Refractive index of a surrounding medium</td>
</tr>
<tr>
<td>$n_{cl}$</td>
<td>Cladding refractive index</td>
</tr>
<tr>
<td>$n_{co}$</td>
<td>Core refractive index</td>
</tr>
<tr>
<td>$P(0)$</td>
<td>Incident optical power</td>
</tr>
<tr>
<td>$P(z)$</td>
<td>Optical power along an optical waveguide</td>
</tr>
<tr>
<td>$P_{ph}$</td>
<td>Light intensity incident at a photodiode</td>
</tr>
<tr>
<td>$R$</td>
<td>Bend radius, reflectivity, resistance</td>
</tr>
<tr>
<td>$R_f$</td>
<td>Feedback resistor value (in a transimpedance amplifier circuit)</td>
</tr>
<tr>
<td>$S$</td>
<td>Responsivity of a photodiode</td>
</tr>
<tr>
<td>$T$</td>
<td>Power transmission coefficient (Fresnel transmission coefficient), Transmisson factor</td>
</tr>
<tr>
<td>$t$</td>
<td>Time, transit of a ray of light</td>
</tr>
<tr>
<td>$t_{max}$</td>
<td>Maximum transit of a ray of light to cover a distance $z$</td>
</tr>
<tr>
<td>$V$</td>
<td>Electrical voltage</td>
</tr>
<tr>
<td>$v_i$</td>
<td>Volume fraction of compound i</td>
</tr>
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\(V_o\) Output voltage
\(w_i\) Weight fraction of compound \(i\)
\(x\) Distance
\(x_i\) Mole fraction of compound \(i\)
\(z\) Distance
\(z_p\) Half way period of a ray propagating along an optical waveguide
AC Alternating current
ADC Analog-to-digital converter
ANN Artificial neural network
ATR Attenuated total reflection (or reflectance)
BPM Beam propagation method
CCS Constant concentration algorithm
CRDS Cavity ringdown spectroscopy
cw continuous wave
DAC Digital-to-analog converter
DC Direct current
DEFC Direct ethanol fuel cell
DLFC Direct liquid feed fuel cell
DMFC Direct methanol fuel cell
DTFI Discrete time fuel injection
FBG Fibre bragg grating
FIB Focused ion beam
FIR Far-infrared
FLRDS Fibre loop ringdown spectroscopy
<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>HRI</td>
<td>High refractive index (coating)</td>
</tr>
<tr>
<td>ICCS</td>
<td>Interpolation algorithm for CCSs</td>
</tr>
<tr>
<td>IDT</td>
<td>Inter-digital transducer</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LPG</td>
<td>Long-period grating</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>m</td>
<td>Molality</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly (a component of DLFCs)</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-electro-mechanical systems</td>
</tr>
<tr>
<td>MIR</td>
<td>Mid-infrared</td>
</tr>
<tr>
<td>MLR</td>
<td>Multi-linear regression (calibration model)</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>OSC</td>
<td>Orthogonal signal correction (calibration transfer procedure)</td>
</tr>
<tr>
<td>OTDR</td>
<td>Optical time domain reflectometer</td>
</tr>
<tr>
<td>PAD</td>
<td>Pulsed amperometric detection</td>
</tr>
<tr>
<td>PCA</td>
<td>Principle component analysis (calibration model)</td>
</tr>
<tr>
<td>PCS</td>
<td>Polymer clad silica (optical fibre)</td>
</tr>
<tr>
<td>PDS</td>
<td>Piecewise direct standardisation (calibration transfer procedure)</td>
</tr>
<tr>
<td>PGA</td>
<td>Programmable gain amplifier</td>
</tr>
<tr>
<td>PLS</td>
<td>Partial least squares (calibration model)</td>
</tr>
<tr>
<td>POF</td>
<td>Plastic optical fibre</td>
</tr>
<tr>
<td>RDS</td>
<td>Ringdown spectroscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>RIU</td>
<td>Refractive index units</td>
</tr>
<tr>
<td>SAW</td>
<td>Surface acoustic wave</td>
</tr>
<tr>
<td>SCS</td>
<td>Silica clad silica (optical fibre)</td>
</tr>
<tr>
<td>SH-SAW</td>
<td>Shear-horizontal surface acoustic wave</td>
</tr>
<tr>
<td>SMA</td>
<td>SubMiniature version A (optical connector type)</td>
</tr>
<tr>
<td>SMF</td>
<td>Single mode fibre</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>SRI</td>
<td>Surrounding refractive index</td>
</tr>
<tr>
<td>TFBG</td>
<td>Tilted FBG</td>
</tr>
<tr>
<td>TIR</td>
<td>Total internal reflection</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet (wavelength range)</td>
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1 Introduction

With the invention of the hydrometer (or hydroscope) by Greek scholar Hypatia of Alexandria\(^1\) around the year 400, the first scientific device was created that allowed for the rough quantification of a fluid’s physical property, the specific gravity (or density). The instrument consisted of a sealed floating stem that sunk the deeper into a liquid solution the less dense it was.

Over the centuries, advanced forms of Hypatia’s hydrometer emerged with different scales according to their desired uses. From an alcohol strength determination perspective, the earliest comprehensive work, according to Lachmeyer et al. \(^{[1]}\), was published by French chemist Joseph Luis Gay-Lussac in 1824 \(^{[2]}\), where he described an alcoholometer based on a hydrometer with a \(\%\)vol (volume percent) scale.

In contemporary sensor systems the densitometric method described by Gay-Lussac still is the quasi-standard for quality monitoring of alcoholic drinks with the difference that hydrometers were widely replaced by state of the art electronic density sensors (section \(2.1\)). Optical methods such as infrared spectroscopy, however, increasingly penetrate this application area because all constituents contained in a beverage can be quantified at the same time using this method (section \(3.3\)).

Today, fluid monitoring is essential in the most diverse range of applications including the chemical industry, biochemical applications, the mentioned beverages industry and drinking water quality control for instance. With the invention of the direct liquid feed fuel cell (DLFC), another domain that shows an ever growing demand for fluid monitoring sensors has emerged which will be briefly addressed in the following chapter.

1.1 Motivation

The primary intention of this investigation is the development of a sensor that allows for the quantification of the known compounds in a binary liquid mixture or to quantify a single compound in a multi-compound mixture of more than two constituents. An example for the latter is the determination of the ethanol content in alcoholic drinks.

\(^{1}\)http://www.inventions.org/culture/female/hypatia.html
beverages which, besides the ethanol, contain a multitude of other components such as acids, sugars and other alcohols (section 3.3). Especially small breweries rely on cheap sensor solutions to monitor the alcohol content of the brew during and after fermentation as they cannot afford appropriate spectroscopic instruments.

The other field that strongly influenced the selection of the fluids that are used in this investigation to evaluate the developed sensor probe is the area of DLFCs which undoubtedly will have a huge impact on the way energy is stored in future, for both low and high powered applications. To date quite a few different types of DLFCs have emerged, each of which is designed to operate with a specific type of fuel (usually a 2-compound mixture) that must be monitored to ensure optimal operating conditions. The most common types are listed in table 1.1 along with their key properties, i.e., the type of fuel, the molecular weight of the fuel substance, the overall cell voltage and the specific energy of the cell.

<table>
<thead>
<tr>
<th>DLFC</th>
<th>Fuel</th>
<th>$M_w$ (g/mol)</th>
<th>$n$</th>
<th>$E^0$ (V)</th>
<th>$E_{sp}$ (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBFC</td>
<td>(Sodium)borohydride</td>
<td>37.74</td>
<td>8</td>
<td>1.64</td>
<td>9295</td>
</tr>
<tr>
<td>DDMFC</td>
<td>Dimethoxymethane</td>
<td>76.10</td>
<td>16</td>
<td>1.23</td>
<td>6931</td>
</tr>
<tr>
<td>DDEFC</td>
<td>Dimethyl ether</td>
<td>46.07</td>
<td>12</td>
<td>1.20</td>
<td>8377</td>
</tr>
<tr>
<td>DFC</td>
<td>Ethanol</td>
<td>46.07</td>
<td>12</td>
<td>1.15</td>
<td>8028</td>
</tr>
<tr>
<td>DEGFC</td>
<td>Ethylene glycol</td>
<td>62.07</td>
<td>10</td>
<td>1.22</td>
<td>5268</td>
</tr>
<tr>
<td>DFAFC</td>
<td>Fornic acid</td>
<td>46.03</td>
<td>2</td>
<td>1.40</td>
<td>1630</td>
</tr>
<tr>
<td>DHFC</td>
<td>Hydrazine</td>
<td>32.05</td>
<td>4</td>
<td>1.62</td>
<td>5419</td>
</tr>
<tr>
<td>DMFC</td>
<td>Methanol</td>
<td>32.04</td>
<td>6</td>
<td>1.21</td>
<td>6073</td>
</tr>
<tr>
<td>DMPFC</td>
<td>1-Methoxy-2-propanol</td>
<td>76.10</td>
<td>16</td>
<td></td>
<td>5635</td>
</tr>
<tr>
<td>DMFCDP1FC</td>
<td>1-Propanol</td>
<td>60.10</td>
<td>18</td>
<td>1.13</td>
<td>9070</td>
</tr>
<tr>
<td>DMFCDP2FC</td>
<td>2-Propanol</td>
<td>60.10</td>
<td>18</td>
<td>1.12</td>
<td>8990</td>
</tr>
<tr>
<td>DTOFC</td>
<td>Tetramethyl orthocarbonate</td>
<td>136.15</td>
<td>24</td>
<td></td>
<td>4725</td>
</tr>
<tr>
<td>DTMFC</td>
<td>Trimethoxymethane</td>
<td>106.12</td>
<td>20</td>
<td></td>
<td>5051</td>
</tr>
<tr>
<td>DTFCC</td>
<td>Trioxane</td>
<td>90.08</td>
<td>12</td>
<td></td>
<td>3570</td>
</tr>
</tbody>
</table>

The overall important property of a fuel is its specific energy $E_{sp}$ as it describes the amount of energy that can be stored in a substance with respect to its weight. It is proportional to the number of electrons $n$ involved in the chemical reaction and the overall cell voltage $E^0$ and inversely proportional to the molecular weight $M_w$ of the substance ($E_{sp} = nE^0/M_w$). Hence, the specific energy of a compound is the greater the more electrons are involved, the higher the cell voltage, and the smaller the molecular weight. The specific energy of hydrogen for instance, which is the most popular fuel of gas based fuel cells, is 32802Wh/kg which is far greater than that of any of the liquid fuels in the table due to the very small molecular weight of
1 Introduction

hydrogen. However, due to issues with the production, storage and distribution of hydrogen liquid fuels are preferable alternatives.

The main advantage of fuel cells becomes evident when comparing their specific energies with those of batteries as shown in figure 1.1.

![Figure 1.1: Comparison of the specific energies of some common batteries and the liquid fuels methanol (DMFC) and ethanol (DEFC)](http://www.e-sources.com/fuelcell-DMFC.htm)

The basic working principle of a DLFC and the reason why it is mandatory to accurately control the fuel concentration will be briefly explained on the basis of a direct methanol fuel cell (DMFC) as it is the most advanced type of all DLFCs. A schematic of the cell structure and its working principle is shown in figure 1.2.

![Figure 1.2: Schematic of a DMFC](http://www.e-sources.com/fuelcell-DMFC.htm)

A fuel cell assembly generally consists of three layers, two outer slabs, called electrodes, and an electrolyte layer in between them. The two electrodes, i.e., the anode

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2http://www.e-sources.com/fuelcell-DMFC.htm
and the cathode, are used as catalysts for the chemical reaction that takes place inside the cell. In the case of a DMFC, methanol is oxidised at the cell’s anode in the presence of water, generating carbon dioxide and water by releasing hydrogen ions and electrons. The hydrogen ions travel through the electrolyte which at the same time is impermeable for the electrons. By establishing an external electrical link between anode and cathode the electrons can flow to the cathode to react with the hydrogen ions and oxygen to water, completing the circuit. This process takes place as long as the anode is fed with fuel.

One of the most challenging problems in operating DMFCs is the so called methanol crossover which means the diffusion of methanol through the membrane from the anode to the cathode, resulting in a positive potential on the cathode side and therefore in a reduction of the overall cell voltage. Both the cell voltage and methanol crossover increase with the methanol concentration. At a certain point though the crossover causes a greater drop in the cell voltage than it is increased by the increasing methanol content. Consequently, there is a methanol concentration at which the cell voltage reaches its maximum. There is ongoing research into new membrane materials with better crossover properties such as Nafion® but the crossover issue has not been solved to date.

For that reason, the methanol concentration in the liquid feed must be continuously monitored and regulated to maintain an optimum working condition.

1.2 Fluids used in this investigation

As mentioned in the previous section, the selection of fluids used to evaluate the developed sensor probe was primarily based on the needs that emerged with the invention of DLFCs. The most advanced types use aqueous solutions of ethanol, methanol, 1-propanol and 2-propanol as fuels. In addition to those alcoholic mixtures, acetone was chosen as a fifth reference fluid as it has similar optical properties as ethanol (with regard to the refractive index, section 5.1.3).

Apart from their usage as fuels, all of the fluids are also frequently applied in the chemical industry, mainly as solvents themselves and for cleansing purposes. The nomenclature that applies to each liquid contains a set of alternative names out of which the most common acronyms are listed in in table 1.2 along with their chemical formulas and two physical parameters, i.e., density and molar mass, which are needed in the following section to transform different quantity measures into one another.
Table 1.2: Physical properties of the pure fluids: acetone, methanol, ethanol, 1-propanol, 2-propanol, and water at 20°C.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Frequent acronyms</th>
<th>Chemical formula</th>
<th>Density (g/cm³)</th>
<th>Molar mass (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>Carbinol</td>
<td>CH₃OH</td>
<td>0.7918</td>
<td>32.03</td>
</tr>
<tr>
<td></td>
<td>Methyl alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wood alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>Absolute alcohol</td>
<td>C₂H₅OH</td>
<td>0.789</td>
<td>46.06</td>
</tr>
<tr>
<td></td>
<td>Ethyl alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methylcarbinol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>Propan-2-one</td>
<td>C₃H₆OH</td>
<td>0.7925</td>
<td>58.08</td>
</tr>
<tr>
<td></td>
<td>Dimethylformaldehyde</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Propanol</td>
<td>Propan-1-ole</td>
<td>C₃H₇OH</td>
<td>0.8034</td>
<td>60.1</td>
</tr>
<tr>
<td></td>
<td>Propyl alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethylcarbinol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Propanol</td>
<td>Isopropanol</td>
<td>C₃H₇OH</td>
<td>0.786</td>
<td>60.1</td>
</tr>
<tr>
<td></td>
<td>Isopropyl alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Hydrogen oxide</td>
<td>H₂O</td>
<td>1</td>
<td>18.01528</td>
</tr>
<tr>
<td></td>
<td>Hydrogen hydroxide</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Other physical properties of the above fluids such as their permittivities, viscosities, speeds of sound and heat capacities, are referred to in the appropriate conventional sensors review sections in chapter [2].

1.3 Definition of terms

In order to quantify compound concentrations in liquid solutions different terms are frequently used in literature, typically expressed in units of weight, volume, or moles[4]. The corresponding definitions are given by equations [1.1] to [1.5] [6].

\[ \text{Molarity } M = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (1.1) \]

\[ \text{Molality } m = \frac{\text{moles of solute}}{\text{Weight of solvent (kg)}} \quad (1.2) \]

[4]The mole is defined as the amount of substance of a system that contains as many elementary entities (e.g. atoms, molecules, ions, electrons) as there are atoms in 12 g of carbon-12 (¹²C) [6]
1.4 Sensor requirements

Depending on the application area, one or more of the above terms are preferably used. In the context of labeling alcoholic drinks the use of volume percent (%vol) is mandatory in the European Union [7]. In solution chemistry the most commonly used units are mole fraction (%mol), weight fraction (%wt) and Molarity (M). The reason for this is that those measures are based on weight and therefore allow for the exact quantification of the respective compounds prior to and after mixing. The volume of a solution, on the other hand, may not necessarily equal the sum of the compound volumes prior to mixing, due to volume contraction or expansion effects. In that case, the deviation from ideality (solution volume = sum of compound volumes) is called excess volume. Those excess properties of the liquid solutions used in this investigation were investigated by several authors, e.g., Bae and Song for aqueous acetone [8], Benson and Kiyohara for aqueous ethanol, methanol and 1-propanol [9] and Saleh et al. for 2-propanol [10].

The different units can be cross converted when the molar mass and/or the density of the pure compounds are known (in the case of molarity the volume of the solution must be known as well).

The tolerances by which the alcoholic strength of different types of alcoholic beverages may differ from the labeled values are regulated by European Union directives and are listed in table 1.3.

The minimum tolerance to be found in the the table is 0.3%vol. Since the sensing method that is typically used is based on density measurements, the tolerance values are related to the overall alcohol strength of the beverage which is mainly ethanol but can also includes small amounts of methanol for instance, as pointed out by Lachenmeier and coworkers [11]. However, the required sensor resolution is clear (<0.3%vol) and the range of concentrations to be monitored depends on the beverages of interest, e.g. up to about 8%vol in the case of beers, up to 16%vol in the case of wines and above 25%vol for spirits.

In the context of fuel cells, the optimum fuel concentration can be easily determined by monitoring the cell’s output power density for varying alcohol concentrations [12].
Table 1.3: Tolerances by law in alcoholic strength for labeling alcoholic beverages in the European Union, as summarised in [1].

<table>
<thead>
<tr>
<th>Beverage</th>
<th>Tolerance (%vol)</th>
<th>EU commission directive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beers (≤ 5.5%vol)</td>
<td>0.5</td>
<td>87/250/EEC [7]</td>
</tr>
<tr>
<td>Beers (&gt; 5.5%vol)</td>
<td>1.0</td>
<td>87/250/EEC [7]</td>
</tr>
<tr>
<td>Wine</td>
<td>0.5</td>
<td>607/2009/EC [11]</td>
</tr>
<tr>
<td>Bottled wine (&gt;3 years),</td>
<td>0.8</td>
<td>607/2009/EC [11]</td>
</tr>
<tr>
<td>(semi-)sparkling wine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beverages containing</td>
<td>1.5</td>
<td>87/250/EEC [7]</td>
</tr>
<tr>
<td>macerated fruit or parts of</td>
<td></td>
<td></td>
</tr>
<tr>
<td>plants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spirits and not otherwise</td>
<td>0.3</td>
<td>87/250/EEC [7]</td>
</tr>
<tr>
<td>specified beverages</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this case the optimum fuel concentration depends on several cell parameters as well as the operation mode so that there is no constant value that is valid for all cells but in general it is up to 3M (<10%wt) for passive cells and about 5M (16.7%wt) for active cells which are operated using external fuel pumps or other auxiliary devices [13]. The resolution of most of the reported methanol sensors is about 0.1M (section 2.6) which corresponds to a weight fraction of 0.32%wt. The conversion between molarity and weight fraction were calculated with regard to equations 1.1 and 1.5 and the physical parameters listed in table 1.2. After appropriate rearrangement of the mentioned equations the conversion can be written as

\[
\%wt = x_1 = \frac{nM}{\rho_{sol}} \times 100
\]  

(1.6)

where \(x_1\) is the weight fraction of the compound of interest, \(n\) the number of moles of that compound in the solution, \(M\) the molarity and \(\rho_{sol}\) the density of the solution which is

\[
\frac{1}{\rho_{sol}} = \frac{x_1}{\rho_1} + \frac{x_2}{\rho_2}
\]  

(1.7)

where \(x_2 = 1 - x_1\).

Further requirements for the sensor include long term stability to avoid frequent re-calibration or even sensor replacement and since the potential range of applications may include the monitoring of flammable liquid solutions, it should not contain any electrical contacts or components. Furthermore, small sensor dimensions and low production and operational costs are mandatory for a low financial impact on the destined application. Finally, a fast response time (<1s) is required with regard to potential real time fluid monitoring systems.
1.5 Fibre-cavity requirements

As for the fibre-cavity also developed in this investigation, it is not targeted at a particular application but considered applicable to a variety of fibre sensors. Such cavities allow optical fibre sensors to be operated in a so called ringdown scheme which essentially is based on an optical signal passing a sensor element multiple times and thus increasing the sensors sensitivity without affecting its properties. A detailed description of the ringdown principle is given in section 3.5.

The requirements for the fibre-cavity are therefore independent of the sensor element and the intended application. However, they mainly include a low insertion loss which is the key property that separates the proposed fibre-cavity from conventional ones, low reflection losses at the cavity boundaries, and reliability over a wide wavelength range to ensure applicability to a large number of sensing purposes, i.e. different fluids. This, as well, is discussed in further detail in section 3.5.

1.6 Thesis outline

Due to the large number of different fluid concentration sensor approaches, their review is split into two chapters. In chapter 2 general sensor configurations based on non-optical monitoring techniques are introduced and assessed on their sensitivity, response time, miniaturisation potential, long term effects and cross sensitivity. The sensor techniques discussed include those that measure density, permittivity, viscosity, ultrasonic velocity, heat capacity, electrochemical quantities as well as sensor-less estimation strategies.

Chapter 3 introduces fibre-optic fluid concentration sensors based on infrared spectroscopy and evanescent field absorption. In the case of the latter, the evanescent wave phenomenon is explained, followed by a description of the basic sensor principle which exploits that phenomenon. Different improved sensor approaches are then introduced that are based on coated fibres, deformed fibre cores or otherwise manipulated optical waveguides. In addition, the drawbacks of contemporary ringdown fibre-cavities are discussed in this chapter.

A theoretical treatment of straight and bent evanescent field sensors and ringdown cavities is given in chapter 4. The influences of the fibre core diameter, the numerical aperture of the fibre, the bend radius and the surrounding refractive index on the sensitivity of different sensor probes are simulated. Afterwards, analytical descriptions are derived for the decay time constants of conventional ringdown cavities and the novel design.
The fabrication processes, measurement setups and results of the two separate investigations are presented in chapter 5. The dependencies derived in the theory chapter are experimentally verified and the advantages of the novel sensor designs are highlighted.

Finally, in chapter 6 the achievements and conclusions of this investigation are summarised. Based on the experimental results, several recommendations for improvements are given with regard to future works on the topic.
2 Conventional fluid concentration sensors review

There is a multitude of physical properties that vary with regard to the composition of a liquid solution such as its density, permittivity or viscosity. In this chapter general fluid concentration sensor principles are reviewed that have proven to be suitable for the purpose of fluid monitoring with a focus on the aqueous solutions of acetone, ethanol, methanol, 1-propanol and 2-propanol, as they are later used to evaluate the novel sensor probe.

2.1 Density sensors

The density $\rho$ (rho) of a substance or material is defined as mass per unit volume (e.g. kg/cm$^3$). When expressed in multiples of the density of some other material, usually water or air, the dimensionless terms relative density or specific gravity apply.

The densities of the solutions under investigation vary considerably with the compound concentration as shown in figure 2.1. A monotonically decreasing relationship for all the binary mixtures enables concentration monitoring over the entire composition range.

![Figure 2.1: Density of aqueous acetone, ethanol, methanol, 1-propanol, and 2-propanol versus solute concentration at 20°C][13][16]
2.1 Density sensors

State of the art fluid density sensors are based on MEMS (Micro-Electro-Mechanical Systems) which integrate sensors and actuators together with electrical and mechanical elements on a common silicon substrate through micro-fabrication technology. This technology makes complete and cost effective systems-on-a-chip possible.

Such a MEMS based density sensor is manufactured by ISSYS (Integrated Sensing Systems) and has been tested on diluted methanol solutions in a series of publications [17–25]. It basically comprises of a micro-fluidic chip where the liquid passes through a resonant silicon U-shaped micro-tube. Changes in the fluid composition, e.g., mass or density, result in a shift of the resonant frequency of the tube which can be acquired using a gain-phase analyzer. A 4-digit density resolution is reported for that sensor which corresponds to approx. 0.05%wt alcohol concentration and an integrated on-chip platinum temperature sensor allows for appropriate sensor calibration. Figure 2.2 shows a cross-sectional schematic of the sensor and the U-shaped micro-tube.

![Image](image.png)

(a) Cross-sectional diagram.  (b) U-shaped microtube.

Figure 2.2: Schematics of a MEMS based U-bend tube resonator as used for methanol sensing [17].

Another commercially available series of density sensors (L-Dens density transmitters), distributed by a company called Anton Paar[^1] is based on the same working principle and manufacturing process and offers the same sensitivity. Osorio et al. [26] used a sensor of that series to determine the ethanol concentration in wine stills.

Besides the single U-shape tube design, there are improved double-loop tubes resulting in more balanced vibrations. Enokson et al. applied such a silicon double-loop tube density sensor to aqueous 2-propanol solutions and reached a sensitivity of 200 ppm (kg/m³). In another paper the same authors investigated the influences of in/anti-phase bending and torsion of the tubes as well as different tube wall thicknesses [27]. Along with other coworkers, Enokson later reported a simplified design using a straight hexagonal vibrating tube which achieved an only slightly lower sensitivity of 256 ppm [28].

[^1]: www.anton-paar.com
There is a great number of further density sensor principles which cannot be addressed in detail due to space limitation. MEMS-type sensors, however, are considered state-of-the-art. They are very compact and cost effective but according to Zhao et al. [6] they are cross sensitive to CO\(_2\) bubbles in fluids and their sensitivity does not satisfy the requirements needed to operate fuel cells at optimum conditions. As the ISSYS and L-Dens sensors are clearly advertised for use in direct methanol fuel cell (DMFC) and direct ethanol fuel cell (DEFC) applications, the latter conclusion of Zhao et al., i.e. the cross sensitivity to CO\(_2\) is not negligible, appears questionable.

### 2.2 Permittivity sensors

The permittivity \(\varepsilon\) (epsilon) of a medium is a measure of its ability to be polarized when exposed to an electric field, expressed in farads per meter (F/m). In other words, it is a measure of the ability of a medium to resist the formation of an electric field within. Thus, the greater the permittivity the higher the resistance to electric fields. Materials of high permittivity (high polarisability) are referred to as dielectric. Usually dielectric properties are described by a single dimensionless term, the dielectric constant \(k\), which is the ratio of a material’s permittivity \(\varepsilon\) and the one of vacuum \(\varepsilon_0\) (8.85 x \(10^{-12}\) F/m). The dielectric constant is therefore also known as the relative permittivity of a material. It is an important parameter for the design of capacitors for instance.

When mixing two substances, the resulting dielectric constant of the solution varies with the compound concentration. Thus, capacitive sensors are suitable for fluid concentration monitoring. The static dielectric constants of the five alcohol solutions used in this investigation are shown in figure 2.3. Static in this context means the response to a direct current (DC) signal.

A drawback of the DC technique, as used to determine the mixing ratio of gasoline and methanol by Maeda [31], is electro-corrosion of the electrodes due to methanol absorption. As a result of the corrosion process dissolved metal ions in the fuel attach to the negative electrode causing a non-negligible change in its capacitance properties. To overcome that issue, Nogami et al. [32, 33] covered the positive electrode by an electrically insulating film and used pulsed signals rather than a DC level.

Bao et al. [34] went one step further and used alternating current (AC) signals which further reduced the effect of corrosion in conjunction with insulated electrodes.

Doerner et al. [35] applied the AC technique to a methanol fuel sensor using a solid teflon® shell packaged into a stainless steel fitting. The reported dielectric spectra
2.2 Permittivity sensors

Figure 2.3: Relative static dielectric constant of aqueous acetone, ethanol, methanol, 1-propanol, and 2-propanol versus solute concentration at 25°C [29, 30].

show flat regions down to the sub megahertz frequency range for which the authors achieved an accuracy of 0.2%wt methanol for concentrations below 5%wt [35].

Figure 2.4: Capacitive sensor configuration by Doerner et al. [35].

Earlier, McKee and Johnson [36] used permittivity measurements at high frequencies to determine the ethanol content in water and glucose using a flow-through s-shaped micro-strip resonator. With the sensor being centered at 900 MHz a resolution of 0.35%vol was reported.

Santos [37] measured the ethanol content in gasoline using a coaxial transmission line comprising of an external hole conductor and an internal center wire. He focused his investigations on the sub gigahertz range since the dielectric constant of the mixtures varies strongly with the ethanol concentration in that range while the influence of gasoline is minor. Unfortunately, no sensor resolution or accuracy were reported.
As a last example, Skierucha and Wilczek \[38\] recently reported a two-wire stainless steel electrode assembly for permittivity measurements of soils in the 10-500 MHz range. Calibration measurements were carried using distilled water, acetone, methanol, and 2-propanol as reference liquids.

2.3 Viscosity sensors

The viscosity, \( \eta \) (eta) is the quantity that describes a fluid’s resistance to flow (thickness), measured in pascal second (Pa·s). The less viscous a fluid the faster it moves when external stress is applied. The theory behind it is that there are multiple layers in the flow which move at different velocities and the viscosity is derived from the shear stress between the layers. Thus, it is defined as the ratio of the shearing stress (F/A) to the velocity gradient (du/dy). Figure 2.5 illustrates the underlying principle.

\[ \text{Figure 2.5: Laminar shear of a fluid between two plates. Friction between the fluid and the moving boundaries causes the fluid to shear. The force required for this action is a measure of the fluid’s viscosity } \] \[39\].

The viscosities of the diluted alcohols of interest versus alcohol concentration at 20°C are shown in figure 2.6. It is clear that high resolution measurements around the flat areas (peak viscosity values ±5% alcohol content) are hardly possible but the slopes in the lower and higher concentration ranges allow for the determination of alcohol contents in those areas.

In order to describe the approach of sensing viscosity two patents are referred to. Cowper’s device measures the pressure drop of the fluid under a controlled flow rate in a vertically disposed, inverted U-tube \[42\] whilst Baldauf and Preidel proposed a differential pressure drop measurement across a constriction where the fluid is pumped through \[43\]. Both approaches are based on the fact that the pressure drop of a fluid is inversely proportional to its viscosity according to the Hagen-Poiseuille law \[44\].
2.4 Ultrasonic velocity sensors

The effect exploited by ultrasonic velocity sensors is that the speed at which sound travels through a given material (medium) depends on the medium’s density and elasticity. The term ultrasonic thereby refers to the frequency range that is being used, i.e., above 20kHz. By measuring the time that such an acoustic signal needs to cover a known distance through a medium, the corresponding sound velocity can be calculated.

There are two major sensing principles using this effect distinguished by the way the acoustic signal interacts with the medium.

A quite straightforward method is to use some sort of pipe with a transmitter on one side and a receiver on the opposing side. Consequently, the speed of sound in this configuration is the ratio of the transmitter/receiver distance to the propagation time of the signal.

This technique was used by Rabinovich et al. [45] in order to monitor the methanol content in the liquid feed of a DMFC at a reported resolution of 0.1%wt for concentrations below 5%wt (by weight). A commercial sensor, distributed by Murata Manufacturing Co., Ltd. [46], has a reported resolution of about 0.02%. Sun et al. [47, 48] investigated the propagation delay rates for temperature between 25°C and 78°C and a methanol concentration range of 0-15%wt at varying transducer dis-
stances. They found the rate of change in the speed of sound to be highly dependent on the methanol content at 25°C but decreasing towards higher temperatures crossing the zero sensitivity line at at 63°C no matter how much the methanol concentration changed which was referred to as the blind region.

The second principle is based on so called shear-horizontal surface acoustic waves (SH-SAWs) which means the propagation of horizontally polarised acoustic waves on the surface of a substrate in between a transmitter and a receiver. So called inter-digital transducers (IDTs) are used to efficiently generate and detect SAWs on a piezoelectric substrate (crystal). One of the IDTs acts as an input, converting electrical voltage variations to mechanical SAWs (transmitter). The other IDT acts as a receiver, converting these mechanical vibrations back to an electrical signal. It has been found that SAW devices react to changes in physical conditions in the propagation path by changes of both amplitude and phase velocity. The propagation path is the mentioned delay line between input and output IDT. Furthermore, changes in environmental conditions lead to changes in the boundary conditions for SAW propagation and hence to a variation in the wave velocity, amplitude, frequency or phase.

Figure 2.7 shows the concentration dependent speed of sound of the fluids under scope at certain frequencies and temperatures. A reversal of the slopes from rising to falling velocities around 20% alcohol content makes sensing difficult in that area but the ranges below and above the turning points are well suited for concentration measurements.

Figure 2.7: Ultrasonic velocity of aqueous acetone at 64.36MHz, 30.6°C [49], ethanol at 10MHz, 20°C [50], methanol at 31.6MHz, 25°C [51], 1-propanol at 5MHz, 20°C [52], and 2-propanol at 10MHz, 20°C [52] versus solute concentration. The graph summarizes the data found in the given references.
The advantage of the SH-SAW method is that the acoustic signal does not have to pass through the liquid to be detected on the other side of a pipe for instance but the liquid only has to be in contact with the propagation path of the SAWs resulting in a very simple planar sensor design as shown in figure 2.8.

![Figure 2.8: Simplified schematic of a SH-SAW sensor consisting of the substrate, input and output IDT and a SAW propagation path in between them](image)

Commonly the propagation path is coated with a material that increases the interaction with the substance to be measured and additional reflectors are used to avoid signal overlaying [54].

SH-SAW sensors usually consist of a reference path and one or more sensing paths and have been used in a variety of biological [55–57] and chemical [53, 54, 58] sensor applications. One of the key elements of SH-SAW sensors is the substrate the transducers are built upon. There are numerous publications on the investigation of the wave propagation properties of different substrates with various cuts and rotation angles as reviewed by Yamaguchi [59].

Penza and Cassano [60] tested different materials on their SAW propagation properties with respect to their sensitivity to methanol, 2-propanol and their binary mixture.

Kondoh et al. [61–63] monitored diluted methanol solutions with an accuracy of 0.1%wt using an SH-SAW sensor operated at a temperature of 60°C.

Ultrasonic velocity measurements are affected by CO₂ bubbles as the propagation speed in the gas is different to the one in the fluid. The achievable resolution is proportional to the propagation path length, thus, reaching high sensitivity somehow contradicts the great potential of miniaturisation of SH-SAW devices.

### 2.5 Heat capacity sensors

The heat capacity of a given amount of a substance is the quantity of heat required to raise its temperature by 1K usually measured in Joule per Kelvin (J/K). The term molar heat capacity defines the heat capacity per unit mole (J/mol K) of a substance whereas the term specific heat capacity describes the heat capacity per unit mass.
(J/kg K). Besides Joule, the calorie (cal/g) and the British thermal unit (btu/lb) are also often used as units of energy. Figure 2.9 shows the molar excess heat properties of the aqueous solutions of ethanol, methanol and 1-propanol. Excess heat thereby means the deviation from ideality (linearity).

![Excess molar isobaric heat capacity of aqueous ethanol, methanol, and 1-propanol solutions versus solute mole fraction at 25°C.](image)

**Figure 2.9:** Excess molar isobaric heat capacity of aqueous ethanol, methanol, and 1-propanol solutions versus solute mole fraction at 25°C [64].

The temperature dependence of the heat capacity of aqueous alcohol mixtures has been investigated by several authors. Benson and d’Acry [65] compared the empirical excess heat capacities for ethanol, methanol, and 1-propanol at 15°C and 35°C. Demirel and Paksoy [66] used that data to evaluate their algorithm that calculates the excess heat properties of the same mixtures for an extended temperature range from 12°C to 37°C. An even wider range was from 5°C to 95°C was investigated by Origlia-Luster and Woolley [67] who determined the molar heat capacities of ethanol, 1-propanol, and 2-propanol.

A heat capacity based methanol concentration sensor was proposed by Baldauf et al. [68] who measured the temperature difference of the liquid after supplying it with a known amount of energy at a constant flow rate. A change of about 2°C was reported for an increase of the methanol content from 0.5M to 1M at a flow rate of 100ml/min.

Heat capacity sensors are insensitive to metallic ions in the fluid and its pH value [6] but the process of heating the mixture is quite slow and thus a major drawback of this technique if a fast sensor response is required.
2.6 Electrochemical sensors

The development of electrochemical fluid concentration sensors hugely benefited from the increasing interest in direct liquid feed fuel cells (DLFCs). The growing demand for methanol sensors has caused a dramatic boost of research activity in this field. The working principle of electrochemical sensors in this context is identical to the one of fuel cells which means that it is based on the measurement of the alcohol concentration dependent oxidation current. Such sensors are therefore also referred to as amperometric sensors.

Throughout the last two decades a series of publications and patents described the methanol oxidation process at a platinum-ruthenium (Pt/Ru) electrode as well as methods on how to quantify the oxidation current as a measure for the alcohol concentration in the liquid feed [69–82].

Figure 2.10 shows a schematic of an electrochemical methanol sensor as reported by Narayanan et al [72]. The fundamental construction is, as mentioned above, identical to that of, in this case, a conventional direct methanol fuel cell (DMFC) comprising of two electrodes coated with Pt/Ru (anode) and platinum (Pt, cathode) and a Nafion®-117 membrane in between the electrodes. The membrane and electrodes are commonly referred to as membrane electrode assembly (MEA). The oxidation of methanol at the Pt/Ru cathode occurs under a constant anodic potential and it was shown that the resulting electrical current is dependent on the methanol concentration in the liquid feed. Changes in the methanol content as small as 0.01M (mol) could be resolved [72] using this method.

![Figure 2.10: Schematic of an electrochemical methanol concentration sensor](image)

Sun et al. [78] incorporated two such MEAs (twin MEA) into their electrochemical sensor device with the result of increased sensor reliability due to the presence of
two current signals. Apart from twin MEAs the authors used a pulsed amperometric detection (PAD) scheme in order to keep the electrodes clear from absorbed species. A sensitivity twice as high as in potentiostatic mode was reported accompanied by an increased stability of the overall sensor signal. However, the sensor’s response time of about 10-50s could not be decreased with this configuration [78]. Geng et al. [82] later reported a similar approach with both electrodes being of identical structure and simultaneously fed with methanol.

Focusing on a faster response time, Qi et al. [75] proposed a simpler, miniaturised sensor configuration using a flexible multilayer design wrapped around a tube that the fuel flows through. In doing so, they managed to reduce the response time to 10-15 seconds. Additionally, they proved that a higher operating temperature results in a stronger oxidation current and hence in greater sensitivity which is true for all sensors based on the electrochemical principle. This, at the same time, means that the sensitivity decreases as one approaches room temperature.

Another approach to miniaturization was proposed by Lee et al. [79]. They reduced the sensor dimensions to 5×5 millimeters by omitting the gas diffusion layer which usually provides an interface for the reactant and product gases to and from the electrodes.

Yang et al. [80] found that the platinum layer thickness has an impact on the current response with the latter being stronger the thinner the Pt layer, which is on a sub-nanometer scale. Accordingly, the sensitivity increases with decreasing layer thickness. In another paper the same authors replaced the Pt layer by a Pt dot design and H-grid electrodes. The magnitude of the response current of this structure was less than in their previous approach but it was expected to result in a higher sensitivity as the grid dimensions become narrower [81].

Besides the large number of publications focusing on methanol sensors, there is also increasing interest in using the amperometric sensor principle in order to determine the ethanol content in a liquid mixture. The key element here as well is the catalyst material on the electrodes which must allow oxidation of the ethanol. Promising results were reported for enzyme modified electrodes [83], nickel/metal oxide composite electrodes [84], platinum-based alloy electrodes [85], platinum/metal oxide composite electrodes [86] as well as nano electrodes to increase the catalyst specific active area [87]. However, a detailed description of the chemistry behind the electrolysis at each of the catalysts is beyond the scope of this summary.

Recently, Tao et al. [87] reported an amperometric ethanol sensor based on state-of-the-art nano technology with detection limits of 6µM in the case of pulsed amperometric detection and 10µM in the case of potentiostatic mode.
Despite their satisfying sensitivity and the efforts in making electrochemical sensors more compact and efficient, a major downside still is the slow response time of at least 10s to step concentration changes which makes real time concentration monitoring difficult. Another handicap is their insensitivity at room temperature and more importantly, the use of electrochemical sensors is confined to the very fluids their electrodes were designed for.

2.7 Sensor-less estimation strategies

As a last type of fluid monitoring techniques, sensor-less estimation algorithms are worth addressing as increased research has occurred in this area as well. Generally speaking, sensor-less means that the fluid under scope is not monitored directly but its concentration is estimated using datasets or algorithms based on pre-calibration measurements. Thus, sensor-less monitoring techniques are intended to reduce the cost and complexity of systems where fluid concentration monitoring is required.

In order to estimate the methanol content in the liquid feed of a fuel cell system for instance, the cell’s key operating parameters such as the open circuit potential, the potential difference between inlet and outlet at known methanol concentrations can be predetermined and appropriately correlated when operating the fuel cell at a later stage [88]. Other parameters suitable for being monitored during operation are the fuel temperature and the electrical current generated by the fuel cell [89].

Sudo [90] proposed a dual sub-stack cell version which comprises of two identical fuel cells connected in series with the outflow of the first cell being the inflow of the second. The indicator for the methanol concentration in this configuration is the voltage difference between both cells.

A fourth method, reported by Chiu and Lien [91], is based on a three-dimensional measurement space, monitoring the electrical current, the voltage and the temperature of a direct methanol fuel cell (DMFC). The proposed interpolation algorithm is based on constant concentration surfaces (ICCS algorithm) which can be determined by spanning three measurement axes with the three mentioned independent variables of a fuel cell system (current, voltage, temperature). For a specific methanol concentration, a series of I-V curves can be acquired with each of them corresponding to a certain temperature resulting in a three-dimensional surface as shown in figure 2.11.

For any unknown methanol concentration level, the measurements of current, voltage and temperature of the fuel cell system result in a specific point in the measurement space. By determining the distance from a predetermined surface, the concentration difference can be calculated. If two or more of those surfaces were
Figure 2.11: A constant concentration surface (CCS) of a DMFC in a three-dimensional measurement space [91]. Several I-V curves were acquired for different temperatures at 5% vol methanol concentration.

pre-acquired, an interpolation algorithm based on those CCSs can be employed to estimate unknown concentrations accurately. It was shown that the estimation error with four CCSs was about ±0.3% vol [91].

However, all the above strategies are vulnerable to fuel cell degradation with respect to its performance, i.e., changing operating parameters with time, environmental influences and/or others. Thus, the pre-determined calibration parameters become inaccurate as indicated by a letter from the reviewer to the authors [92].

Chang et al. [93, 94] reported a portable DMFC system with an integrated sensor-less methanol content regulation for a constant load. The method they used is called impulse response based on discrete time fuel injection (IR-DTFI) which is not supposed to be affected by any performance degradation. It is based on a pre-determination of the maximum cell power and the corresponding current \( I_{max} \). Based on the latter, a minimum specific monitoring period is defined which the fuel can sustain the load \( I_{max} \) for when supplied by a specific amount of fuel. A specific amount of fuel will then be injected into the anode flow circuit measuring one operating parameter (voltage, current, or power) twice during the previously defined period. Depending on an up or down trend detected, additional fuel is injected or not. However, this method may be susceptible to dynamic operating conditions such as voltage and current drifts as presumed by Ha et al. [95], but later the same authors extended their algorithm for driving dynamic loads by adjusting the monitoring period at runtime when the changes in the operating conditions exceed a certain threshold [96, 97].

Ha et al. [95] came up with their own version of sensor-less methanol monitoring, claimed not to be affected by degradation or dynamic influences as well as it
is supposed to be independent of the load that is applied to the fuel cell output. Their algorithm targets the methanol consumption rate which depends on the electrical current (load) and the operating temperature. A database with experimental methanol consumption values for various operating conditions allows for the selection of the correct consumption rate from current and temperature measurements at runtime. That value is then used to control the cell supply with methanol of a constant concentration. However, the weak point of this procedure is that the methanol concentration cannot be determined, so if the real concentration for any reason deviates from the pre-defined value then the algorithm results in wrong predictions and thus in an inaccurate control of the feed stream.

Recently Shen et al. [98] adopted and modified the CCS based algorithm of Chiu and Lien [91] considering cell degradation. However, Chang et al. [97] propose that its application may be as well limited whenever the fuel cell system is subjected to dynamic loads.

## 2.8 Summary

In table 2.1, an evaluation of important parameters of each of the sensor types reviewed in this chapter is presented. The parameters of major interest are sensitivity, cross sensitivity, response time, long term effects, and miniaturisation capabilities. In terms of sensitivity and response time, the best values found in literature were considered. Other parameters such as the complexity of a sensor design and its cost were not considered because most of the referenced approaches are not commercially available but prototypes.

<table>
<thead>
<tr>
<th></th>
<th>Sensitivity(^1)</th>
<th>Cross sensitivity(^2)</th>
<th>Response time(^3)</th>
<th>Long term effects(^4)</th>
<th>Miniaturisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Permittivity</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Viscosity</td>
<td>?</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Ultrasonic velocity</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>?</td>
<td>+</td>
<td>-</td>
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<tr>
<td>Electrochemical</td>
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<tr>
<td>Sensorless estimation</td>
<td>-</td>
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<td>-</td>
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<td>+</td>
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</tbody>
</table>

\(^1\) (+) < 0.1%wt
\(^2\) (-) Cross sensitive to gas bubbles, metallic ions etc. (temperature is excluded)
\(^3\) (-) Sensor degradation, inability to compensate for changing environmental conditions.
\(^4\) (+) < 1s
Apart from the sensitivity, a fast response time is a key parameter of real time fluid monitoring systems. Electrochemical type sensors in particular suffer from a slow response as do the sensor-less approaches that are based on such electrochemical devices. Additionally, both have issues with membrane degradation and catalyst deterioration. The group of slow sensors also includes the heat capacity and viscosity types which makes them unsuitable for real time operations as well. Faster sensors not only allow for a rapid detection of changes in the fluid’s composition but also enable data averaging resulting in improved signal to noise ratios. It is therefore not surprising that the greatest sensitivities were reported for the group of faster responding sensors, i.e., density and ultrasonic velocity types.

In terms of miniaturisation, the electrochemical sensors offer advantages over the physical sensing methods as their structure is comparably simple. However, with the introduction of MEMs technology physical sensors became more attractive for compact applications. In the case of portable devices, sensor-less estimation strategies are the best choice in terms of cost and occupied space as there are no separate sensor elements. However, they may require frequent re-calibration.

With respect to dynamic range, the density and permittivity type sensors are well suited as they uniquely allow fluid monitoring over the entire concentration range while the the other physical sensors show non-monotonic relationships between the respective physical property and the compound concentration. Electrochemical sensors are the worst in this category with a quite narrow sensing range.

Some kind of cross sensitivity applies to most of the sensor types (CO₂ bubbles, metallic ions, etc.). Only viscosity and heat capacity sensors are marginally effected or immune in that regard. The cross sensitivity to temperature was not taken into account as most sensor solutions are calibrated against temperature.
3 Fibre-optic fluid concentration sensors review

The sensor technologies reviewed in the previous chapter have all demonstrated severe limitations, particularly if required for real-time concentration measurements and when the fluid under test is flowing. Optical fibre sensors offer a viable alternative to this as optical measurements are ideally instantaneous.

Following a very brief introduction to and classification of fibre-optic sensors, the focus of this chapter is on fibre-optic sensor principles suitable for fluid concentration monitoring, in particular on evanescent field sensors as the developed sensor probe is based on this sensing method. However, a very brief overview of infra-red absorption fluid concentration sensors is given first as the method is widely applied. Finally, ringdown spectroscopy principles are reviewed with regard to the developed fibre-cavity.

3.1 Introduction

The first optical fibre sensors emerged in the 1970s as advances were made in optical sources, low-loss optical fibres, and optical detectors, originally developed for optical communication purposes. It soon turned out that fibre-optic sensors have certain advantages over conventional sensors such as immunity to electromagnetic interference, lightweight, high sensitivity, small size, large bandwidth, biocompatibility, high fusion point, water and corrosion resistance, passive operation and ease in implementing multiplexed or distributed sensors. Initially, the main application areas were harsh environments for which conventional sensors were not well suited. Nowadays, optical fibre sensors can be found for almost every kind of purpose, e.g., temperature, humidity, pH, strain, force, pressure, displacement, vibration, acceleration, rotation, current, gas sensing and many more. New technologies such as in-fibre Bragg Gratings, interferometers, novel fibre types and nano technology were driving forces for the penetration into increasingly new application areas such as bio-sensing. There are several reviews on the subject, e.g., multidisciplinary sensors [99,101], op-
tical chemical sensors \[102\] as well as an exhaustive bi-annual review of chemical and biosensors \[103\]–\[107\].

### 3.2 Sensor classification

Basically, all types of optical fibre sensors comprise an optical source, a modulation zone, an optical receiver and optical fibre links between them. The modulation zone represents the sensing point at which the source signal is manipulated in amplitude, phase, frequency, polarisation, or other parameters dependent on the measurand.

Optical fibre sensors are commonly divided into two main categories, intrinsic and extrinsic sensors. In the case of intrinsic sensors, the light is modulated whilst still being guided within the fibre whereas in the case of extrinsic sensors, the light exits the fibre and is modulated in a separate zone before being relaunched into either the same or a different fibre. Figure 3.1 illustrates both types of sensors. This investigation concentrates on a third category, i.e., a sensing principle known as evanescent field sensing which can incorporate properties of both intrinsic and extrinsic sensors by allowing some of the light energy to escape from the fibre core into the surrounding medium (figure 3.1). A more detailed description of evanescent field sensors is given in section 3.4.

![Figure 3.1: Optical fibre sensors can be categorised as either an intrinsic or extrinsic. Evanescent field sensors have features of both categories.](image)

Figure 3.2 shows a sub-classification of intrinsic and extrinsic sensors as proposed by Jasenek \[109\]. It is clear from figure 3.2 that a single purpose sensor, e.g., temperature measurement, can be assigned to more than one subgroup as several tech-
3 Fibre-optic fluid concentration sensors review

(a) Intrinsic sensors.

(b) Extrinsic sensors.

Figure 3.2: Subgroups of intrinsic and extrinsic sensors.
niques can be used for that purpose. However, there are quite a few other ways to categorise optical fibre sensors, e.g., based on the modulation process (intensity, phase, frequency, polarisation, wavelength), the application area (physical, chemical, biomedical, etc.), the underlying physical effect (refractiometric, interferometric, absorption, scattering, etc.), the type of measurement (point, multiplexed, distributed, quasi-distributed) and so on.

Ning et al. proposed a 3-D Cartesian coordinate scheme to classify optical sensors based on the type of fibre, the light source and the modulation scheme \[110\]. Each of these categories is further subdivided as shown in figure 3.3 allowing for any sensor to be assigned to a distinct point in the 3-D space. The publication also includes references to some of the approaches mentioned above.

![Figure 3.3: 3-D optical fibre classification scheme according to the type of fibre, the light source, and the type of modulation \[110\].](image)

The classification of optical fibre sensors remains an ongoing task as new technologies emerge, e.g. Photonic Chrystal Fibres (PCF), and new sensing methods, e.g. Brilloon Optical Time Domain Analysis (BOTDA), are being proposed.
3.3 Infrared absorption sensors

The term absorption spectroscopy incorporates all spectroscopic techniques that measure the absorption of radiation of a sample as a function of frequency or wavelength. The infrared (IR) range of the electromagnetic spectrum is commonly divided into the near-, mid-, and far-infrared region (see table 3.1 for corresponding wavelength ranges $\lambda$, frequencies $\nu$ and wavenumbers $\bar{\nu}$).

IR radiation can excite molecular vibration, rotation, and motion including various subtypes causing so called absorption features, peaks or bands in the IR transmission spectrum of a substance. There are three types of such absorption bands: overtones, combinations, and difference bands. Overtones are multiples of the fundamental absorption frequency of a substance caused by molecules being excited from ground to higher-energy states. Vibrationally coupled frequencies are referred to as combination bands while difference bands result from the difference between interacting bands. The resulting IR absorption pattern of a sample is unique to that sample’s molecular structure. Thus, measuring the IR transmission spectrum allows for the identification of the sample and, in most cases, for the quantification of its compound composition.

The experimental setup in its most basic form comprises of a beam of IR radiation directed to a sample where the wavelength dependent intensity of the radiation that passes through the sample is measured. Infrared absorption spectroscopy is predominately applied to gases and vapours of fluids but can also be used to determine fluid quantities directly.

In the early years of commercial development (circa 1980) of absorption spectroscopy solutions, the NIR region was most frequently used for sensing purposes as optical components were widely available at reasonable prices compared to mid- and far-infrared components.

The NIR absorption spectra of the aqueous solutions under scope in this investigation were published by various authors, e.g. [111, 112].

Application wise, the high demand for alcohol sensors by the beverages industry to monitor fermentation processes continuous to be a major driving force for the

<table>
<thead>
<tr>
<th>Table 3.1: Regions of the infrared electromagnetic spectrum.</th>
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<td>Wavelength $\lambda$ (µm)</td>
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<td>--------------------------</td>
</tr>
<tr>
<td>NIR</td>
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<tr>
<td>MIR</td>
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<td>FIR</td>
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</table>

$\nu=\nu/c$ (c=300,000km/s), $\bar{\nu}=100/\lambda$
development of such sensor solutions using a multitude of calibration algorithms, e.g. [113–127].

The mid-infrared (MIR) wavelength region offers greater absorption features for many fluids. On the other hand, greater absorption means lower transmission which, in practice, requires absorption cells of considerably smaller dimension, usually less than 0.1mm in length. Another problem arises from strong background absorption of water in that wavelength area. However, both issues were addressed by multiple authors in the context of fermentation monitoring [1, 128–138].

A detailed review of the particular techniques employed is well beyond the scope of this literature review but the sheer number of publications is, however, a good indication for the high demand of appropriate sensor solutions in that industry.

It can be concluded that IR absorption spectroscopy is a reliable and accurate method for the identification and quantification of diluted alcohols. Moreover, it allows for the determination of other constituents present in fluid solutions. Those so-called chemometric measurements allow for the derivation of fingerprints of those mixtures. On the other hand, spectroscopic interferences between highly concentrated compounds and those of lower concentration can make the discrimination between them difficult, especially in the MIR spectral [139].

According to Zhao et al. [6], the drawback of IR absorption based methods is their susceptibility to CO\(_2\) or other bubbles in the liquid mixture causing the peak absorption wavelength to shift, thus limiting the sensor resolution. Therefore, most of the above authors degassed the fluids using filter paper or by ultrasonication prior to the acquisition of their absorption spectra.

A significant drawback of all the above methods is their lack of speed. Even though no sample preparation is required for most of the reported estimation procedures, an average time of one to two minutes is required to obtain reliable results.

### 3.4 Evanescent field sensors

Evanescent field absorption spectroscopy is based on attenuated total reflection (ATR) that occurs at the boundary between two dielectric media. In the context of optical fibre sensors, one of the media is an optical waveguide which is surrounded by another medium of lower refractive index, the cladding or an absorbing medium that is to be monitored. Under certain circumstances which will be addressed in this chapter and in greater detail in the next chapter, a guided ray of light penetrates the evanescent field, that extends beyond the fibre core, at each point of reflection. The result is
a decline in the ray amplitude (attenuation) dependent on the surrounding medium which makes this phenomenon suitable for sensing purposes.

In the following several evanescent field sensor approaches are reviewed. In that context the limitations of straight fibre probes are highlighted followed by a description of different methods on how to increase the sensitivity of such a basic sensor geometry, i.e., selective ray launching, coated fibre probes, fibre tapers, bent fibres and D-fibres. In particular, the straight probe, selective ray launching and bent fibres are the basic principles used for the derivation of an effective absorption coefficient for the developed evanescent field sensor later in section 4.1.

3.4.1 Principle

In order to use an optical fibre effectively as an evanescent field sensor its cladding has to be partly or fully removed in the sensing region of the fibre so that the exposed fibre core is surrounded by or in close proximity to the absorbing medium of interest. Light is launched into one end of the fibre and detected at the other end. In order to propagate along the fibre core, a light beam has to undergo total internal reflection (TIR) at the core/cladding or core/medium interface, respectively. TIR occurs when the angle of the incident beam with the normal to the core/cladding interface is greater than the so called critical angle. Incident beams at angles smaller than the critical one will be partly reflected and partly refracted, loosing intensity at every point of reflection (until extinction) as shown in figure 3.4.

Figure 3.4: In order to undergo total internal reflection, the angle of the incident light beam with respect to the core/cladding interface has to be greater than the so called critical angle. Rays of incident angles smaller than the critical one undergo partial refraction and partial reflection. The images are edited versions of the ones in [140].

Once a ray of light undergoes total internal reflection, the superposition of the incident and the reflected rays forms a standing electromagnetic wave whose electric
3.4 Evanescent field sensors

field amplitude extends beyond the fibre core, called the evanescent field, which exponentially decays with distance from the interface. This decay actually gave the evanescent field its name which literally means 'vanishing' or 'fading away' [141]. Figure 3.5 shows such a standing wave and the resulting evanescent wave and its interaction with a sample medium.

![Figure 3.5](image_url)

The optical power detected at the end of the waveguide depends on the amount of absorption of the evanescent field as the variable figure (it also depends on losses due to the fibre itself but those losses are considered constant, independent of the surrounding medium). The term attenuated total reflectance or reflection (ATR) used in this context describes this loss of power. The evanescent field absorption for a given length of the unclad fibre depends on the number of reflections per unit length and the penetration depth of the evanescent field into the sample medium. The penetration depth in turn is related to, amongst others, the refractive index of the medium which means that any change in the index of refraction around the exposed fibre core (in certain boundaries) has an immediate impact on the detected optical power at the end of the waveguide. This is why evanescent field sensors are predominantly used as refractive index sensors and the refractive index of the surrounding medium is commonly referred to as surrounding refractive index (SRI). Apart from the determination of the refractive index, the obtained attenuation in the optical signal can also be related to the absorption coefficient of the surrounding medium so that proper calibration allows for the identification of that very substance or for the quantification of a diluted substance in a known binary mixture.

Over the years, several types of evanescent field sensor probes have emerged, mainly classified by their geometry or shape such as tapers, bent fibres and side-polished probes. Figure 3.6 shows a collection of possible sensor configurations of which the most frequently used ones are discussed in the following section.
3.4.2 Straight probe

The most straightforward form of an evanescent field sensor is a straight uniform unclad optical waveguide. A typical experimental setup is shown in figure 3.7 comprising an optical source, a microscope objective (MO) or some other lens focusing the light onto the fibre tip, the fibre including an unclad region and an optical power meter or detector at the distal end. The unclad region of the optical waveguide is enclosed by an absorption cell that contains the absorbing medium. The intensity level detected at the other end of the fibre is dependent on, amongst other parameters, the absorption of the surrounding fluid and thus an indicator for the compound concentration in a liquid solution.

Paul and Kychakoff [144] were one of the first authors who, in 1987, reported the use of standard multimode fibres for the measurement of evanescent field absorption as a function of refractive index and bulk absorption coefficient of different organic substances. The optical fibres used where 50µm in diameter with unclad sections ranging from 10cm to 28.5cm in length. Until then, prisms had been predominantly used for coupling the light into and out of the medium.

Around the same time silver-halide fibres were utilised as evanescent field sensor elements, mainly in a spectroscopic context due to better MIR properties compared to normal glass fibres. This way ATR spectroscopy overcame the issue of strong
absorption in the IR and the need for tiny absorption cells as the bulk amount of optical power is retained inside the waveguide. Simhony et al. [145] for instance acquired IR spectra of acetone/water and glycine/water mixtures using a 10cm long unclad fibre region of 900μm in diameter. Two kinds of ATR cells were reported, one containing a single fibre and another containing a bundle of seven fibres for increased sensitivity. With the latter, acetone concentrations of 1% could be resolved. In later publications the authors extended their investigations to protein solutions [146], organic solutions [147] and water only [148].

Until today, many authors have reported the use of such simple straight sensor probes for absorption measurements of different liquid mixtures, e.g., chlorine/water [149, 150], dye solutions [151–153], chloride/isopropanol [154] and oils [155]. However, it was evident that the sensitivity was limited but could be increased by changing the fibre geometry and/or by coating the unclad fibre core with a substitute cladding material which caused a rapid uptake in the number and range of applications and thus in the number of publications. The reason for the relatively low sensitivity of straight probes is given by the fact that, in practice, the refractive index of the medium to be monitored is usually smaller than that of the original cladding which means that the numerical aperture (NA) of the sensing region is greater than that of the fibre itself. Consequently, the critical angle of the sensing region cannot be reached by the light beams propagating along the fibre core and thus no significant evanescent field penetration takes place (see section 4.1 for more details).

In the following section, several methods are discussed that are frequently used to increase the sensitivity of a straight and uniform sensor probe.

### 3.4.3 Selective ray launching

Selective ray launching or selective mode excitation means that only rays at a certain angle are injected into a multimode fibre in order to have only rays close to the critical angle propagating along the fibre core. This can be achieved either by spatially filtering the collimated beams of an optical source, using an annular beam mask as proposed by Ruddy et al. [156] or by rotating the fibre end face with respect to the source beam as reported by Gupta et al. [157]. Both authors compared their results to the unfiltered launching condition.

Figure 3.8 shows the setup used by Ruddy et al. [156]. The annular beam mask can be seen in the bottom right corner. Polymer clad silica (PCS) fibres of 200μm and 600μm in diameter with a numerical aperture of 0.4 were used for the experiment. Intensity profile measurements revealed that incident angles of 70° to 72.5°
and absorption measurements of aqueous methylene blue dye were conducted in the visible spectral range.

Figure 3.8: Schematic of the annular beam mask setup used by Ruddy et al. for the selective injection of rays into a multimode fibre [156].

As expected, the 200µm probe showed a higher sensitivity than the 600µm probe as there are more reflections per unit length (see figure 3.9). Additionally, the bulk absorption in a 1cm long cuvette is shown to highlight the nonlinear dependence in the case of evanescent field absorption. However, a comparison with the theoretical absorbance of a straight probe (600µm) with non-filtered launching conditions resulted in a 200-fold increase in absorbance for a methylene blue concentration of $10^{-6}$ when injecting rays of bespoke angles only which is called into question when compared to the reported sensitivity increases of other authors below.

Figure 3.9: Absorbance of aqueous methylene blue versus dye concentration. (1) Evanescent sensor probe: 20.5cm unclad 200µm PCS fibre. (2) Evanescent sensor probe: 22cm unclad 600µm PCS fibre. (3) Bulk absorbance: 1cm cuvette [156].

Figure 3.10 shows the configuration used by Gupta et al. [143] where a rotation stage allows for the adjustment of the fibre for the desired launching angles with respect to the optical source.
The authors also used aqueous methylene blue as the absorbing solution but in addition to a straight probe a tapered one was also investigated (see section 3.4.5 for details on tapers). The fibre core diameter in both cases was 600\(\mu\text{m}\) with a numerical aperture of 0.17 and a 8cm long unclad region in the case of the straight probe and 1.5cm in the case of the tapered probe, respectively. The operating wavelength was chosen to be 632.8nm. The small numerical aperture calls for a small critical angle of just under 10° but due to the short length of the fibre (15cm) rays of greater launching angles could be injected which would disappear following longer distance propagation (due to refraction losses). The authors found that the absorbance peak correlated to a launching angle of 24°. Figure 3.11 shows the absorbance of both sensor types for unfiltered and filtered launching conditions.

Taking the absorbance of the uniform probe in an unfiltered condition at a methylene blue concentration of 10\(\mu\text{Mol}\) as a reference, the authors concluded that the unfiltered taper configuration is 2.36 times as sensitive, the filtered uniform probe 2.89 times and the filtered taper 7.55 times.

Dubois et al. [158] described the effect of selective mode excitation in graded index multimode fibres but for sensing purposes step index fibres are by far the dominant fibre type.

### 3.4.4 Coated fibre probes

In order to increase the sensitivity of optical fibre sensors with regard to changes in the surrounding refractive index (SRI), the unclad region of the fibre core is often coated with a variety of polymers or metals dependent on the application purpose.
3 Fibre-optic fluid concentration sensors review

Figure 3.11: Absorbance of aqueous methylene blue versus dye concentration. (left) unfiltered launching. (right) filtered launching (20°). [157].

Polymers

The configuration of polymer coating of optical fibres is shown in figure 3.12. The coating’s refractive index is only slightly less than that of the fibre core but greater than that of most fluids so that the evanescent field can penetrate the coating effectively. For that reason, such coatings are commonly referred to as high refractive index (HRI) coatings. A sample gas or liquid can diffuse into the coating and cause a change of the optical properties of the coating by means of it’s refractive index. The diffusion process into the coating as well as the substance’s removal when the concentration decreases are time dependent so the sensor response time is often an issue. An example is the detection of propane gas through a teflon coating reported by Ruddy and McCabe [159].

Figure 3.12: Unclad fibre core region coated with a porous cladding for gas sensing [143].

Such porous polymer claddings can also be used to increase the sensitivity of evanescent field sensors in the IR region. In section 3.3 it was stated that the background
absorption of water in the mid-infrared spectral region limits the detection of species with weaker absorption in that wavelength area. Certain polymer claddings allow the diffusion of organic compounds but block out water so that its strong absorption features are “invisible” for the sensor. Krska and Kellner [160, 161], for instance, dip-coated a silver halide fibre with low density polyethylene to measure concentrations of chlorinated hydrocarbons in water. In another approach normal glass fibres were coated with polysiloxane (a silicone mixed with a polymer) for the same purpose [162]. The response time for the latter was reported to be 5-10 min.

For certain applications coatings are needed that actually allow the penetration of water rather than blocking it out, e.g., for the measurement of the pH level of fluids [163] or for humidity sensing [164]. So called immobilisers entrapped in the coating account for a change in the absorption of light when the corresponding physical property of a liquid varies. With respect to pH sensors, those immobilisers are often dyes but there are several other immobilisation methods [165] as well which are beyond the scope of this review.

**Metal films**

Refractive indices can be measurement at greater sensitivity using the effect of surface plasmon resonance (SPR) in metal layers coated onto unclad fibre cores. SPR is a complex physical phenomenon that occurs under the condition of total internal reflection but can be explained briefly as follows. When a light beam strikes the thin layer of metal coating (usually not more than some 10s of nanometers in thickness) at a certain incident angle, the resonant angle, then its surface plasmons start to oscillate resulting in the absorption of light. The resonance condition itself depends on the surrounding medium absorbed onto the metal, in particular it’s mass which is proportional to its density and thus its refractive index. In other words, a change in the SRI causes a shift in the resonant angle which in turn affects the attenuation of the light beam striking the metal layer. It is also characterised by a short interaction length being typically only a few micrometer for NIR light.

SPR has been applied to a variety of chemical and biological sensing purposes and proven to be highly sensitive [166]. Mitsushio et al. [167, 168], for example, achieved a resolution of better than 0.0001 refractive index units (RIU) with a gold layer of 45nm in thickness vacuum deposited onto a half a PCS fibre core as shown in figure 3.13. The sensor was tested on, amongst others, aqueous methanol solutions where the reported resolution corresponded to approx. 0.05%vol methanol. The response time was between 30 and 90 seconds, dependent on the alcohol concentration.
Before SPR was applied to optical fibre sensors, prisms were used for the purpose of guiding the light to the interaction layer. Lee and Tsai [169] recently demonstrated interferometric refractive index measurements with a gold coated prism (figure 3.14). They tested their setup on four different aqueous alcohol solutions (without saying which alcohols were used) and reached a sensitivity of $1.5 \times 10^{-6}$ RIU, one of the but highest found to date in literature. The fluids were held stationary for 200 seconds.

Due to the achievable sensitivities of SPR based optical refractive index sensors a great number of publications can be found on the subject applied to both fluid and gas concentration measurements, e.g. [166].

The use of coated optical fibre cores for sensing purposes is often combined with one of the sensitivity increasing methods described in the following subsections.

### 3.4.5 Tapered probe

The principle of evanescent field sensing was explained in section 3.4.1 and it was stated that the sensitivity increases with the penetration depth of the evanescent field and the number of reflections per unit length of the unclad fiber core. The idea behind tapers is to reduce the core diameter in order to increase the number of reflections and to bring the angles of incident beams with the normal to the core/medium interface closer to the critical angle of the sensing region which in turn increases the penetration depth of the evanescent field into the absorbing medium. Figure 3.15 illustrates the
geometry of a tapered fibre and the ray diagram therein. A ray of light arriving to the first taper at an incident angle greater than that of the sensing region does not cause any considerable penetration of the evanescent field. However, the angle decreases with every subsequent reflection and thus comes closer to the desired critical angle. As a result the penetration depth as well as the number of reflections throughout the straight part between the two tapers is increased. The second taper then converts the angles back to their original values to avoid refraction losses on the remaining propagation path to the receiver.

![Ray tracing along a fibre taper](image)

In order to achieve the desired effect, a minimum diameter for the inner fibre core has to be taken into account below which the rays would become wholly refractive (refraction losses). The ratio of the core radii after and before the taper is a characteristic value and referred to as taper ratio. Besides the taper radius, the taper length, and the incident angles, the numerical aperture of the fibre is a key value with regard to the achievable sensitivity as it determines the maximum angle at which light can be launched into an optical fibre.

Besides a linear taper geometry as shown in figure 3.15, it is possible to fabricate different profiles that include curved shapes. Gupta and Singh [170] investigated linear, exponential-linear and parabolic taper geometries (see figure 3.16) with respect to the sensitivity of the different geometries. Of the three, the parabolic-shaped probe was found to have the highest sensitivity followed by the linear and the exponential-linear shapes. A more general description of tapers with regard to the concentration of optical power from a fibre of a large diameter into one of a smaller diameter can be found in [171], (section 5).

However, in the context of optical fibre evanescent field sensors, the first tapers appeared shortly after initial success obtained using straight probes was reported. Tai et al. [172] described a methane gas sensor using a standard multimode step index silica fibre of 50µm in diameter, taper radii ranging from 1.8µm to 7µm and taper lengths of 5-10mm. The minimum detectable concentration of methane was reported to be 1% with a 1.8µm/10mm taper at a wavelength of 3.392µm.

An extensive theoretical and experimental treatment of tapered fibre sensors was published in a series of papers by Gupta et al. [170] [173] [175]. An effective absorption
Figure 3.16: Linear, exponential-linear and parabolic taper profiles according to Gupta and coworkers [170]. The graph shows the taper radii versus the taper length with $\rho_i$, $\rho_o$ and $L$ being the taper input radius, the taper output radius and the taper length, respectively.

coefficient was derived in order to examine the influence of the sample refractive index, the taper geometry, radius and length as well as the numerical aperture and radius of the fibre core on the sensitivity.

Mignani et al. [176] reported a quadrupled absorbance of a tapered sensor compared to a straight uniform probe using a 200$\mu$m PSC fibre. The taper was approx. 11mm in length and 24$\mu$m in diameter and was tested on a liquid solution of cobalt chloride hexahydrate salt in 2-propanol.

A taper used for the determination of methanol and water absorption in the MIR spectral region was reported by Raichlin and coworkers [177]. Made of a 900$\mu$m silver-halide fibre, the sensitivity of the 35mm long taper was proven to increase as the flattened taper radius decreases (down to 190$\mu$m in that configuration).

Tian et al. [178] built an interferometric refractive index sensor, using two tapers in a single fibre at distances of 24mm, 36mm and 55mm. The latter was found to cause a linear wavelength shift of 0.171nm per 0.01 refractive index units.

Tapers are widely used for a diverse range of applications especially when coated with layers of indicator dyes, sol-gels or even metal (see section 3.4.4).
3.4.6 Bent probe

Another way to decrease the incident angle of rays in the sensing region with the normal to the core/medium interface is to bend the fibre at “extreme” angles under exposure to heat such that the stress build up is relieved. Figure 3.17 shows a schematic of a U-bend sensor probe, the most common configuration of a deformed fibre core.

![Figure 3.17: Ray tracing on a bent optical fibre geometry according to Gupta et al. [179].](image)

Following the paths of the two rays shown in the plot it is clear that there are two possible ways of ray propagation within the core. A ray can undergo total internal reflection at only the outer surface or at both the outer and the inner surface which results in a different amount of absorption in each case. The angles throughout the bent area are reduced at both interfaces compared to the angles in the straight part of the fibre, bringing them closer to the critical angle of the sensing region. This is actually dependent on the entry angle a ray undergoes when arriving to the bend. In addition to the absorption due to the evanescent field, further losses occur at the entry point into the bend when a ray strikes the outer surface at a small enough angle (not shown in the figure). A more detailed analytical discussion of the subject is given in section 4.1.4 as the evanescent field absorption sensor probe described in this thesis is based on such a U-shape.

One of the first reported measurements of refractive indices of liquids using bent optical fibres was by Takeo and Hattori [180, 181]. Plastic fibres of 0.5 to 2mm in diameter were bent to radii of 4 to 8mm and the partially unclad core was exposed to different oils [180] and aqueous alcohol and sugar solution [181]. In conclusion, the authors reported a maximum refractive index resolution of three decimal places. The
relatively high inherent loss of plastic fibres, however, limited the application of such sensor probes to comparatively short distances. In order to overcome that limitation, the same authors later used silica core fibres and extended the application area to multi-point fluid monitoring using an optical time domain reflectometer (OTDR) [182]. An OTDR, in short, measures the back-reflection of a fibre versus time which is transformed into a distance and hence allows for the location based monitoring of inherent fibre losses, caused by whatever phenomenon. A multimode silica fibre of 80µm in diameter was bent at radii of 410-655µm at multiple locations along the fibre core, using a CO$_2$ laser as heat source, before the cladding was etched throughout the bent regions.

A “massive” 3mm silica rod, bent to a radius of 15mm, was used to measure the transmission spectra of several organic liquids in the NIR spectral range by Eberl and Wilke [183]. The selection of fluids included, amongst others, methanol and 2-propanol in water. The corresponding spectra were averaged over a period of 30 seconds but still did not obtain considerable sensitivities. It will be shown in section 4.1.4 that the sensitivity of U-bend sensors increases as the fibre core diameter and the bend radius decrease which may be the main reason for the low sensitivity achieved in this approach.

A great contribution with regard to the theoretical and experimental evaluation of U-bend sensors for varying parameters was, again, made by Gupta and different coworkers [154, 179, 184-187]. They investigated the influence of the fibre core diameter, the fibre NA, the bend radius and the SRI on the sensitivity which will be referred to in detail in the sensor theory chapter of this thesis (chapter 4). An experimental verification of the theoretically derived dependencies was carried out using different liquid mixtures such as methylene blue dye in water [179] and cobalt chloride in isopropanol [154, 185]. Coated U-bend sensors were also investigated by the authors in the context pH sensing [184, 186-188]. The joint conclusion of the publications above is that the sensitivity of a U-bend sensor, apart from an optional coating, generally increases with a decreasing fibre diameter, a decreasing bend radius (down to certain radius where cross coupling from the input arm to the output arm of the U-bend occurs), an increasing NA and an increasing SRI (in certain limits). Figures 3.18 and 3.19 show examples of some of the above relationships.

Another group of authors around Lewis, King and Lyons [189-196] extensively investigated U-bend sensor probes in both single and multi-point sensor configurations based on artificial neural network (ANN) pattern recognition calibration techniques. The patterns of acquired OTDR traces of up to five U-bend sensors, exposed to water, ethanol or mixtures of both, were processed by the mentioned techniques to reduce
3.4 Evanescent field sensors

Figure 3.18: Evanescent wave absorption coefficient versus varying concentrations of cobalt chloride in isopropanol for two U-bend sensors (radius=2.5mm) comprising of 300µm PCS fibres with different numerical apertures. [154]. The fibre having the greater NA is more sensitive by means of a greater absorption coefficient for the given U-bend geometry.

Figure 3.19: Evanescent wave absorption coefficient versus bend radius for different concentrations of cobalt chloride in isopropanol using PCS fibres of 300µm in diameter and a numerical aperture of 0.4 [154]. The smaller the bend radius the greater the sensitivity with a lower limit due to cross coupling between both arms of the bend [185].
the cross sensitivity to external parameters such as temperature. In their latest report, the sensors were incorporated into a silica clad silica (SCS) fibre of 62.5µm in diameter and 810 test readings were recorded for nine different combinations of three fixed concentrations of ethanol in water (12.5%, 25% and 50%), in order to train the ANN [196]. Figure 3.20 shows such an OTDR trace of the described multi-point sensor configuration.

![OTDR trace of a 5-point U-bend ethanol sensor configuration](image)

Figure 3.20: OTDR trace of a 5-point U-bend ethanol sensor configuration where the drop in optical power at each sensor location is a measure for the ethanol content [196].

Verma and Gupta [197] carried out theoretical works on the effect of a gold coating on the outer surface area of a U-bend sensor and found it to be more sensitive than a corresponding tapered sensor probe. Recently, such a coated type of U-bend sensor was patented by Caron et al. [198].

The latest modification in the configuration of a U-bend based sensor probe was reported by Nath [199]. In his approach, the optical signal passed the bend twice as one end of the fibre was angled in a way that the light was reflected back into the fibre. Tested on a aqueous propylene glycol solutions, the authors found the double-pass sensor to be up to twice as sensitive as a corresponding single-pass probe (dependent on the SRI).

### 3.4.7 Side-polished probe, D-fibre

Side-polishing an optical fibre has the same effect (although it is weaker) as cladding removal. It is generally applied to singlemode fibres in order to enhance their sensitivity by maintaining structural integrity at the same time. The process results a D-shaped cross section in the transverse view of the fibre as shown in figure 3.21. Even though both terms, side-polished and D-fibre, are often used alternatively, there
is a difference in how both are manufactured. In the case of a side-polished sensor the fibre is glued into a fused quartz block or similar to facilitate polishing (figure 3.21). The fibre is slightly bent with a large radius of curvature in order to only expose a small cross section of the fibre to the absorbing medium. A D-fibre on the other hand is directly drawn from an appropriate preform [200] and maintains its shape throughout the length of the fibre.

Figure 3.21: Side-polished singlemode optical fibre block resulting in a D-shaped cross section [143].

Muhammad et al. [201–205] have worked out the characteristic parameters of such sensor probes which are the core/cladding refractive index difference, the core diameter and the flat surface to core distance. They described the influence of those parameters on the sensitivity to evanescent field absorption and the birefringence properties of the elliptical fibre core which is used for this kind of sensor probe. Having tested their sensors on methane gas and liquid level water monitoring, the authors recommended the application of HRI coatings in order to overcome the low sensitivity of plain D-shaped sensors [202].

In the context of refractive index detection with D-fibres, recent reports mainly use planar waveguides, coated with a variety of metal layers. A zink oxide film, for instance, on top of the residual cladding of thicknesses ranging from 0.8-2.5µm was used by Andreev and coworkers and applied to water, ethanol and water/glycerol solutions in the NIR spectral renage [206]. The detection limit was reported as $2 \times 10^{-4}$RIU.

A comparison of a gold coated D-shaped fibre sensor with an uncoated version was conducted by Yong and coworkers [207]. The sensitivity of the former was found to be approx. 1.5 times that of the later (the value was calculated by the author from the slopes of the corresponding graphs).
3.4.8 Summary

Straight and uniform unclad sensor probes were shown to provide only very limited sensitivity to varying SRIs which can be overcome by numerous methods, e.g., launching only rays at selected angles close to the critical angle into the fibre has some impact. Nonetheless, using deformed fibre cores is more popular because they are easily manufactured and can be combined with other methods such as coatings and/or fibre gratings.

Surface plasmon resonance techniques offer the highest resolution found in literature \(7 \times 10^{-7} \text{RIU} \) \( [208] \). The challenge here is to deposit a uniform coating onto the optical fibres which proves difficult as fibres are of cylindrical geometry. Some authors therefore coated only half the core or simply dip-coated the sensing region if applicable. An advantage of coatings is that they enable the monitoring of chemicals that have low refractive indices such as gases and the coating material can be specifically chosen for the medium to be measured. The downside of using coatings is their slow response time with typical values ranging from 30 to 200 seconds.

Fibre gratings were not reviewed in this context as they are not used in this investigation. However, there are a couple of approaches using gratings in combination with the methods reviewed in this chapter such as tapered \( [209] \), etched \( [210] \) and D-shaped \( [211] \) gratings. The main issue with fibre gratings is that high resolution wavelength detection is not as straightforward as intensity measurements requiring bulkier and more expensive sensor equipment.

3.5 Ringdown spectroscopy

Ringdown spectroscopy (RDS) is an absorption technique based on the fundamentals described in the section about IR absorption sensors (see section 3.3). It was shown that especially in the NIR spectral region, low absorption features offer only limited sensitivity for the quantification of chemical substances. The idea behind RDS is to increase the absorption path length within an absorption cell by confining the latter with highly reflective mirrors on either end. As a result, the optical signal is repeatedly reflected back and forth and thus passes the absorbing medium several times. In this context an absorption cell is referred to as a cavity or optical long path cell which is why RDS is generally referred to as cavity ringdown spectroscopy (CRDS). Besides the increase in sensitivity, CRDS has more benefits such as the immunity to drifts in the optical source intensity which will be addresses in the following section.
3.5.1 Optical long path cells

The first optical long path cell, applicable for the determination of the absorption of trace elements, is due to White [212]. In 1942 he proposed an optical system in which the radiation propagates back and forth through the same volume. The essential parts of his design are three concave mirrors, all with the same radius of curvature, two on one side of the cavity and one on the other side as shown in fig. [3.22]. The only way

![Figure 3.22: Schematic of the optical long path cell proposed by White in 1942 (White cell) [213].](image)

intensity can be lost is by absorption within the cavity or scattering on the reflective surfaces. These losses can be quantified from the remaining intensity acquired at the bottom hole in B. Using this design, White [212] reached optical path lengths of up to 56 meters (90 reflections within an absorption cell of approx. 62.5cm in length).

A different type of cavity was proposed by Herriott in 1964 [214] using only two spherical mirrors facing each other. In contrast to White’s cell the beam enters and leaves the cavity through the same slit in one of the mirrors.

One year later White published an advanced version of his cell using astigmatic mirrors and achieved path lengths of up to 3km [215]. With regards to practical applications he focused on optical delay lines for use in storage and filtering or in other logic and signal processing applications but he also mentioned the capability of measuring small optical losses.

Both the White cell and the Herriott cell are based on measurements of the amount of absorption by determining the intensity of the light that leaves the cavity after several round trips.

The first use of such an optical cavity for measurements of the rate of absorption is widely attributed to O’Keefe and Deacon [216] in 1988 although there is evidence from Russian literature dated back to 1976 where Kornienko and Skuibin [217] proposed that the measurement of the rate of loss of light intensity from an optical cavity can be used to obtain absorption spectra in a similar way.
By measuring the rate of absorption there is no proper exit for the light that’s being launched into a cavity. In fact, the losses within the absorption cell are quantified through the acquisition of the small amounts of light that leak out the cavity through the mirrors at every reflection until the pulse has been totally absorbed. The result is an exponential decay of the detected intensities behind one of the mirrors as shown in figure 3.23 where a single laser pulse was launched into a cavity.

![Exemplary ringdown curve using a pulsed laser source](image)

**Figure 3.23:** Exemplary ringdown curve using a pulsed laser source [218]. The attenuated pulse amplitude peaks are fitted to an exponential decay whose decay time constant is a measure for the absorption within the cavity.

The decay time constant of such an exponential function is a direct measure for the absorption inside the cavity because the higher the absorption the faster the pulse fades out and thus the smaller the decay time constant. The analytical treatment of how to extract this time constant from experimental data and how it relates to the concentration of the substance under scope is given in section 4.2.3.

### 3.5.2 Types of ringdown spectroscopy

Since rate of loss measurements were first described, the technique was further developed and has become one of the key methods for the determination of trace elements. Over the years many subtypes of RDS have evolved out of which the most frequently used and referred to [219–224] are listed below.

- Open path cavity based types
  - CRDS (Cavity ringdown spectroscopy) [225–227]
  - PS-CRDS (Phase-shift CRDS) [228, 229]
3.5 Ringdown spectroscopy

- CE-RDS (Cavity enhanced RDS) \[230, 232\]
- PD-CRDS (Polarisation dependend CRDS) \[233\]
- CL-CRDS (Cavity-locked CRDS) \[234, 235\]
- FT-CRDS (Fourier-transform CRDS) \[236\]
- ICLAS (Intra cavity laser absorption spec.) \[237, 238\]
- ICOS (Integrated cavity-output spectroscopy) \[239, 240\]
- Off-axis ICOS \[241\]
- ...

- Fibre-cavity based types
  - FLRDS - Fibre-loop RDS \[242, 245\]
  - PS-FLRDS - Phase-shift FLRDS \[246\]
  - Grating based \[247\]
  - Mirror based (metallic, dielectric) \[248\]
  - ...

The optical source signal can be either a single pulse which is the most common approach or a continuous wave (cw) where the cavity is pumped up to a certain intensity level before the continuous light beam is quickly interrupted or the cavity is being brought out of resonance, causing the accumulated intensity to be absorbed within the cavity \[249, 255\].

The classification of absorption cells in open-path and fibre-cavities was chosen with regard to the way the light interacts with the absorbing medium. In the case of the former, the light is in direct contact with or directly absorbed by the medium whilst in the case of the latter, the interaction takes place through the evanescent field that surrounds the optical fibre. Fibre-cavities, thus, combine RDS with all the possibilities offered by the evanescent wave sensing principles described earlier in this chapter. However, it should be mentioned that the above discrimination is not exact as there are some fibre-cavities which include an air-gap as the sensing region, e.g. \[242\], but those are the only exception.

Since the focus of this investigation is on a novel fibre-cavity design, only fibre based cavities are reviewed in the following.
3.5.3 Fibre-cavities

In the context of optical fibre interferometers, fibre-cavities were already in use before ring-down techniques began to penetrate the area of evanescent field sensors. Early investigations comprised highly reflective external dielectric mirrors, attached to the fibre ends using index matching gel [256]. Later such mirrors were glued to the fibre ends to reduce the susceptibility to vibration [257–259]. Metallic coatings directly vapour-deposited onto the fibre end faces were then used to reduce mirror coupling/misalignment losses and to further decrease the sensitivity to mechanical vibrations [260, 261]. In similar designs those metallic films were replaced by multilayer dielectric coatings and successfully applied to evanescent-field sensing by several authors. Lerber and Sigrist [248], for instance, used such a mirror based ringdown scheme to monitor the etching process of a single-mode fibre. the cladding became and were able to resolve the optical losses at approx. $4.5 \times 10^{-4}$ dB.

Reflective coatings made from semiconductor materials can achieve a very high reflectivity but are designed for specific operating wavelengths only. Metallic coatings, on the other hand, work over a wider spectral range but are less reflective, especially in the visible wavelength region (see figure 3.24). Good reflectivity values are, however, achievable in the NIR region.

![Reflectivity versus wavelength of some common metals at normal incidence](image)

**Figure 3.24:** Reflectivity versus wavelength of some common metals at normal incidence [262].

To overcome the issue of surface roughness of the fibre ends due to imperfect polishing, coatings were often replaced by Fibre Bragg Gratings as the reflective elements [232, 263].

In another type of fibre-cavity the fibre ends were spliced together forming a fibre-loop where no reflective elements are needed at all. Light was launched into the ring using an optical coupler of high coupling ratio and another coupler diverted a small
amount of the circulating pulse intensity to a detector after each round trip. Fibre-loops offer the same flexibility as straight cavities in terms of applicable fibre types and potential sensor elements to be inserted into the ring.

Figure 3.25 shows the three most commonly used fibre-cavity designs, one based on FBG reflectors, another one using reflective coatings on the fibre end faces and an example of a fibre loop. Out of these, the grating based cavity only works for very narrow range of wavelengths limited by the width of the grating while the other two designs offer much greater bandwidth.

![Common fibre-cavity designs.](image)

In terms of sensor elements for fibre-cavities, a couple of options were proven suitable for a variety applications (figure 3.26). With regard to liquid absorption measurements, multimode fibre-loops with tiny air-gaps (in the \( \mu \text{m} \) range, matching the dimension of the fibre core) were used by multiple authors, mostly tested...
on organic dye solutions at different wavelengths \[242, 243, 246, 266, 266, 267\]. Singlemode fibre loops were also used as temperature \[268\] or pressure \[269\] sensors introducing an FBG into the loop as the sensing element. Plain multimode loops without sensor elements within the loop were applied as force \[270\] and strain \[271\] sensors exploiting the altering loss of the fibre when under pressure/strain.

Evanescent field measurements offer a more efficient way to fluid concentration monitoring since air-gaps introduce large losses and are difficult to align \[265\]. In order to extend the evanescent field into the surrounding medium fibre-tapers \[218, 247, 272\], side-polished fibres \[232\] as well as (pairs of) long period gratings \[263, 273\] were successfully used. The underlying sensing principle of such evanescent sensor probes is explained in sections \[3.4\] and \[4.1\].

### 3.5.4 Summary

A major drawback that all the above approaches have in common is an almost 100% coupling loss when the light is coupled into the various types of passive cavities, either through the reflective layers or due to the high coupling ratio couplers. Since the photo detector is commonly located behind the second mirror of the same reflectivity, a maximum of about \(1/10000\) of the initial pulse intensity can be detected in the case of passive non resonant cavities which further decreases with each round trip. The same is true for using couplers. On the other hand, the high reflectivity or coupling ratios are necessary to achieve large numbers of round trips within the cavity. Thus, pulses of high intensity and highly sensitive photo detectors or optical amplifiers within the cavity are required \[237, 274\]. Although ringdown methods have shown great potential for high sensitivity detection, their use to date has thus been confined largely to the research laboratories. For this reason a novel fibre-cavity was developed for this investigation that reduces those coupling losses.
4 Sensor theory

In the following chapter the theoretical background of evanescent field sensors and ringdown cavities is described. It is based on a ray optics approach rather than the modal propagation of light as absorption phenomena at the interface between two media as well as the reflection at such an interface can be easily described by basic analytical geometry.

First a general classification of rays on an optical waveguide is given followed by an analytical description of the absorption of light through an evanescent field. Those results are applied to a straight evanescent field sensor probe by means of the derivation of an evanescent absorption coefficient which is then further developed for and compared with that of a U-bend sensor. The influence of the fibre diameter, the bend radius and the numerical aperture of the fibre on the sensitivity are investigated.

Finally, the absorption coefficient of a meander-shaped sensor is derived and evaluated for the same parameters showing a significant increase in sensitivity in the case of the latter.

In part two of this chapter the intensity decay of a light pulse in an optical cavity is analytically described starting with a regular ringdown cavity (open path cavity). The findings are then used to derive the decay time constant of the proposed fibre-cavity.

4.1 Evanescent sensor probe

In this section a theoretical evaluation of the proposed meander-shaped evanescent field sensor probe is carried out. A brief classification of rays that propagate along an optical fibre of a certain geometry is given followed by a description of the evanescent field which the sensing principle of this investigation is based on. Afterwards, an evanescent absorption coefficient is derived for the case of straight sensor probes, single bends and multiple bends.
4.1.1 Classification of rays

Classical optical fibre theory has established that it is possible to have different types of rays propagating in multimode optical fibres, each of which having greater or lesser impact on the sensitivity of evanescent sensor probes. In order to distinguish between the different types, the classification below applies throughout this chapter.

**General rays**

When the principle of evanescent field sensors was described in section 3.4.1, it was stated that, provided that the core refractive index $n_1$ is greater than the surrounding refractive index (SRI) $n_2$, rays can be reflected or refracted at the interface between both media and the amount of light energy that is transferred to the refracted or reflected ray is dependent on the incident angle $\Phi_z$. Rays that are totally reflected are commonly referred to as bound rays and the angle at which they become partly refractive is called the critical angle $\Phi_c$. That means that the types of rays can be classified with respect to their incident angles [171].

\[
\text{Refracted rays: } 0 \leq \Phi_z < \Phi_c \quad (4.1) \\
\text{Bound rays: } \Phi_c < \Phi_z \leq \pi/2 \quad (4.2)
\]

By definition, bound rays propagate without loss of energy on a non-absorbing waveguide (total internal reflection). They either cross the fibre axis between successive reflections (meridional rays) or follow a helic path along the fibre core (skew rays) and hence never cross the fibre axis.

Due to their lossy nature, the refracting rays are also referred to as leaky rays. Those rays that are neither bound nor refractive are summarised in a third group called tunneling rays which are of leaky nature as well.

**Rays on a bend**

With regard to the bent fibre probes described later in this chapter, the following types of rays are of interest. Tunneling rays are used to describe the radiation loss at the entry point of a bend. Refracting rays are referred to the refraction loss at consecutive reflections between the inner and outer bend surface and whispering-gallery rays undergo refraction at the outer bend surface only.
4.1.2 The evanescent field

The nomenclature for angles, distances and refractive indices throughout this chapter is based on the schematic in figure 4.1 where a meridional ray is characterised by its launching angle $\Phi_i$, its corresponding incident angle $\Phi_z$ at the core/medium interface, with the normal to the interface, its half way period $z_p$ and its length $L_p$ between two consecutive reflections. The refractive indices $n_0$, $n_1$ and $n_2$ correspond to the launching medium (typically air), the fibre core, and the surrounding medium, respectively, where $n_2$ is typically referred to as $n_{cl}$ when the surrounding medium is the original fibre cladding. Further explanations or characterisations follow at the appropriate locations in the sections below.

![Figure 4.1: Characterisation of a meridional ray as it propagates along an optical fibre core on a zig-zag path. The respective nomenclature is given in the text.](image)

In the context of fibre-optics, an evanescent field is generated at the core/medium interface under the condition of total internal reflection (TIR) (see section 3.4.1). The field thereby extends beyond the fibre core and its magnitude decays exponentially with distance from the core. The electric field component $E$ versus distance $x$ from the core/cladding interface is described by

$$E = E_0 e^{-x/d_p}$$

(4.3)

where $E_0$ is the field’s amplitude at the interface and $d_p$ the penetration depth of the evanescent field into the surrounding medium. A derivation of different forms of this equation from Maxwell’s electro-magnetic field theory can be found in literature at multiple places, e.g., in [275].

The penetration depth is the key parameter when it comes to evanescent field sensors as it describes the amount of interaction with the surrounding medium. It does not describe the maximum penetration, which would be dependent on the detection threshold of the acquisition system being used, but the general point at which the
intensity of the electric field drops to a value of $1/e$ of its amplitude at the interface. The corresponding depth of penetration is defined \[276\] as

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \Phi_z - n_{21}^2}} = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \Phi_z - \sin^2 \Phi_c}}$$  \hspace{1cm} (4.4)$$

where $\lambda$ is the wavelength of the incident light and $n_{21} = n_2/n_1 = \sin \Phi_c$. The remaining quantities are defined in figure 4.1.

It is clear from equation 4.4 that an evanescent field will only penetrate the surrounding medium for incident angles greater than the critical angle as the root expression becomes negative for angles smaller than that. It is also clear that the penetration depth increases as $\Phi_z$ approaches $\Phi_c$ which is a particularly important aspect and therefore shown in figure 4.2 for different surrounding refractive indices (SRIs).

![Figure 4.2: Penetration depth of the evanescent field into the surrounding medium for different SRIs versus the angle of incidence at $\lambda=650$nm and $n_1=1.457$. The chosen SRIs range from the refractive index of water (1.33) to almost the core refractive index.](image)

It can be seen in the figure that the smaller the SRI is the smaller is the critical angle of the sensing region at which the penetration depth yields its maximum (infinity). For greater incident angles, though, the penetration depth dramatically decreases which causes a problem in the detection of chemicals of low refractive indices, e.g. gases and most liquids. The reason for that is that only rays at angles within a certain limit $\Phi_i(\text{max})$ with the normal to the fibre axis can be launched into an optical fibre, a measure which is expressed as its numerical aperture (NA):

$$NA = n_0 \sin(\Phi_i(\text{max})) = \sqrt{n_1^2 - n_2^2} \hspace{1cm} (4.5)$$
The consequences of that limit on the penetration depth can be seen by correlating $\Phi_i(\text{max})$ to the smallest achievable angle of incidence at the core/medium interface $\Phi_z(\text{min})$ through

$$\Phi_z(\text{min}) = \cos^{-1}\left(\frac{n_0}{n_1} \sin \Phi_i(\text{max})\right) = \cos^{-1}\left(\frac{\text{NA}}{n_1}\right)$$  \hspace{1cm} (4.6)

having made use of Snell’s law which describes the angles of incidence and refraction at the interface of two dielectric media as:

$$n_0 \sin(\Phi_0) = n_1 \sin(\Phi_1)$$  \hspace{1cm} (4.7)

If, in a practical example, one uses a multimode fibre of NA=0.2, a minimum value for $\Phi_z$ of about 82° can be achieved. If one now exposes the fibre core to an aqueous solution that has a typical refractive index within the range of 1.33-1.36 then $\Phi_z$ is less than 70° which is not even close to $\Phi_c$. Looking at figure 4.2, it is clear that no significant evanescent field penetration can take place under these circumstances. A fibre with a numerical aperture of 0.4 would bring $\Phi_z(\text{min})$ down to approx. 74° but that still would not be low enough to determine small sample concentrations in aqueous mixtures. Figure 4.3 shows the decreasing gap between both angles for a typical NA range of plasti clad silica (PCS) fibres which are frequently used for the purpose of evanescent field sensing.

**Figure 4.3:** Minimum achievable angle of incidence $\Phi_z(\text{mix})$ of a ray at the core/medium interface with the normal to the interface versus the numerical aperture of an optical fibre. The core refractive index was set as 1.457, a typical value for PCS fibres, and $n_0$ was assumed to equal 1. The critical angle of the sensing region corresponds to an aqueous solution with a refractive index of 1.335.
It is now clear that the range of incident angles that cause a significant penetration of the evanescent field into the surrounding medium is quite narrow and makes the monitoring of aqueous solutions almost impossible when using a straight and uniform fibre.

To put the above dependencies into the context of loss or absorption of optical power, a general expression of the expected sensitivity in the form of an evanescent absorption coefficient will be addressed in the following.

### 4.1.3 Straight probe

Unlike core absorption that can be described along a ray path, power loss due to an absorbing medium that surrounds the fibre core cannot be quantified by simple geometrical optics because the loss occurs beyond the ray path. Since such radiation loss is a wave phenomenon, wave effects must be built into the ray treatment by the assumption that losses only occur at reflection or turning points.

#### An evanescent absorption coefficient

Considering an optical fibre locally unclad and exposed to an absorbing medium, the transmitted optical power can be described as (equation 35-14 in [171])

$$P(z) = P(0)e^{-\gamma z}$$

where $z$ is the distance along the unclad fibre core, $P(0)$ the transmitted power in the absence of an absorbing medium, and $\gamma$ the evanescent absorption coefficient defined as (equation 35-12 in [171])

$$\gamma = NT$$

where $N$ is the number of ray reflections per unit length along the unclad core region and $T$ the power transmission coefficient also referred to as Fresnel transmission coefficient.

According to figure 4.1, the number of ray reflections per unit length in a fibre core of radius $\rho$ is

$$N = \frac{1}{z_p} = \frac{1}{L_p \sin \Phi} = \frac{\cos \Phi}{2\rho \sin \Phi} = \frac{\cot \Phi}{2\rho}$$

and the general definition of the power transmission coefficient is (equation 35-11 in [171]):

$$T = 1 - \frac{\text{Power in reflected ray}}{\text{Power in incident ray}}$$
For the case of strongly guided meridional bound rays \((n_1 >> n_2)\) in the unclad area of a step index multimode fibre, Ruddy [277] reported the transmission coefficient to be

\[
T = \frac{\alpha \lambda n_2 \cos \Phi_z}{\pi (n_1^2 - n_2^2) \sqrt{\sin^2 \Phi_z - n_{21}^2}}
\]  

(4.12)

where \(\alpha\) is the bulk absorption coefficient of the surrounding medium. The form of equation 4.12 may vary with regard to the considered angle, being the incident angle at the core/medium interface with the normal to the interface in this case. However, that angle can be transformed into any other angle of interest. In another publication, Ruddy at al. concentrated on the angle the rays make with the fibre axis [156]. It must be noted that if \(T\) is formulated as dependent on another angle then \(N\) must be transformed accordingly.

However, by substitution of equations 4.10 and 4.12 in equation 4.9 the evanescent absorption coefficient of a single ray can be written as

\[
\gamma(\Phi_z) = \frac{\alpha \lambda n_2 \cos \Phi_z}{2\pi \rho (n_1^2 - n_2^2) \sin \Phi_z \sqrt{\sin^2 \Phi_z - n_{21}^2}}
\]  

(4.13)

where \(\rho\) is the fibre core radius.

With regard to the fibre and surrounding parameters, it is clear from equation 4.13 that the absorption increases as \(n_2\) increases and \(\rho\) decreases. The absorption coefficient is further inversely proportional to the square of the numerical aperture of the fibre (equation 4.5) which means that the greater the NA, the greater is \(\gamma\) as the numerical aperture is always less than one.

**An effective absorption coefficient**

Gupta and coworkers used equation 4.13 to derive an effective absorption coefficient \(\gamma_{eff}\), integrated over all rays for both collimated [173] and diffuse [174] illumination

\[
\gamma_{eff}(\Phi_2, \Phi_1) = \frac{\int_{\Phi_1}^{\Phi_2} p(\Phi) \gamma(\Phi) \, d\Phi}{\int_{\Phi_1}^{\Phi_2} p(\Phi) \, d\Phi}
\]  

(4.14)

where, if the entire fibre end face is illuminated, i.e., all bound rays are allowed to propagate, \(\Phi_1\) and \(\Phi_2\) are the critical angle of the sensing region and \(\pi/2\), respectively, and \(p(\Phi)\) the power arriving at the fibre end face which can be written as

\[
dP_{coll} \propto \frac{n_1^2 \sin \Phi_z \cos \Phi_z}{(1 - n_1^2 \cos^2 \Phi_z)^2} \, d\Phi_z
\]  

(4.15)
Evanescent sensor probe

in the case of collimated illumination \[173\] and as

\[ dP_{\text{diff}} \propto n_1^2 \sin \Phi_z \cos \Phi_z \, d\Phi_z \tag{4.16} \]

in the case of diffuse illumination \[174\].

In the investigation of this the focus is on diffuse illumination as the proposed sensor probe was illuminated using an LED source. Thus, by substitution of equations 4.16 and 4.13 in equation 4.14, the effective absorption coefficient can be written as:

\[
\gamma_{\text{eff}}(\Phi_1, \Phi_2) = \left( \frac{\alpha \lambda n_2}{2\pi \rho (n_1^2 - n_2^2)} \right) \frac{\int_{\Phi_1}^{\Phi_2} \cos^3 \Phi_z \left( \sin^2 \Phi_z - n_{21} \right)^{-1/2} d\Phi_z}{\int_{\Phi_1}^{\Phi_2} \sin \Phi_z \cos \Phi_z \, d\Phi_z} \tag{4.17}
\]

To obtain results that are comparable regardless of the actual bulk absorption coefficient \(\alpha\), the evanescent absorption coefficient \(\gamma\) is commonly normalised to the latter. Numerical calculations of equation 4.17 were carried out in Mathcad® to show the influence of the decisive parameters graphically. Figure 4.4, for instance, illustrates the dependence of the \(\gamma/\alpha\) ratio on the SRI for different fibre core diameters. Again, typical PCS fibre parameters were chosen for the simulation. The numerical aperture was selected to be \(\text{NA}=0.2\) which corresponds to a lower integration limit of \(\Phi_1=82^\circ\). As expected the absorption increases with the SRI and decreases with the fibre core radius. The configuration has an upper detection limit of \(n_2=1.443\) which is the value

\[ \begin{array}{c}
\text{Figure 4.4: Ratio of } \gamma/\alpha \text{ versus the surrounding refractive index for different fibre core radii. The other parameters were set as: } \\
\lambda = 650\text{nm}, \ n_1 = 1.457, \ n_{cl} = 1.443 \ (\text{NA} = 0.2). \ \text{The SRI range shown corresponds to the fluids under scope.}
\end{array} \]
of $n_{cl}$ with respect to the numerical aperture. Consequently, SRIs above $n_{cl}$ cannot be detected.

Figure 4.5 shows the same relationship for an NA of 0.4 ($n_{cl} = 1.401$). In this configuration the critical angle of the fibre is approx. 74° which is about 8° closer to the corresponding critical angle of 68° at $n_2 = 1.335$ but the difference varies with the SRI (figure 4.3). However, the decrease causes the $\gamma/\alpha$ ratio to increase by a factor of 4.7 for the 50µm probe around the water refractive index ($n_2 = 1.335$). The range of detectable refractive indices, however, is now limited to $n_{cl} = 1.401$.

In the case of selected ray launching $\Phi_2$ is commonly set to be only a few degrees larger than $\Phi_1$ so that $\Phi_2 < \pi/2$. It was shown that this principle increases the $\gamma/\alpha$ ratio by a factor of approx. 3, around the refractive index of water (NA=0.4) [173]. It was further shown that illuminating the fibre with a collimated source beam slightly increases the same ratios [170].

The initial assumption of the above two-dimensional treatment was that all guided rays are meridional rays which always cross the fibre axis. Optical fibres, however, are three-dimensional waveguides and most rays are actually skew rays which never cross the fibre axis but propagate on a helical path along the fibre core. The angle at which a ray is reflected in the third dimension is called the skewness angle $\Phi_S$ and in the case of meridional rays that angle is 90°. It was shown that the evanescent absorption of a ray decreases with an increase in skewness so that the above calculations result in an overestimation of the real case. A more detailed discussion of the topic can be found in [278–280]. In the following, however, the two-dimensional approach will

---

**Figure 4.5:** Same as figure 4.4 except for the numerical aperture which is 0.4 in this case.
be carried on with in order to be comparable with other literature data that was gathered using the same analytical method.

### 4.1.4 Bent probes

When a ray of light arrives to a bend then the original incident angle at the core/medium interface in the straight part of the fibre undergoes a transformation at the outer and the inner bend surface, provided the ray strikes the latter which is not necessarily the case (dependent on the angle at which the ray enters the bend). Figure 4.6 shows that transformation graphically for two exemplary rays that enter a U-shaped fibre core at different angles and different distances from the surface.

![Figure 4.6: Ray propagation on a U-shaped sensing region of an optical fibre](image)

Based on the figure, the corresponding transformation equations are given by

\[
\sin \phi = \left( \frac{R + h}{R + 2\rho} \right) \sin \Phi_z \tag{4.18}
\]

\[
\sin \delta = \left( \frac{R + h}{R} \right) \sin \Phi_z \tag{4.19}
\]

where \( R \) is the bend radius, \( \rho \) the fibre core radius, \( h \) the distance of the ray from the inner core surface as it enters the bend, \( \Phi_z \) the original angle and \( \phi \) and \( \delta \) the transformed angles at the outer and the inner bend surface, respectively.

Accordingly, the effective evanescent absorption coefficient \( \gamma_{eff} \) of equation 4.17 must be split into two parts, one for each surface, as shown by Gupta et al. for the case of collimated illumination of the fibre core [179]. For the considered case of
diffuse illumination the absorption coefficient of each bend surface $sf$ can be written as

$$
\gamma_{\text{eff}}(\Phi_1, \Phi_2)_{sf} = \left( \frac{\alpha n_2}{2(2\pi \rho (n_1^2 - n_2^2))} \right) \frac{\int_0^{2\rho \Phi_2} \int_{\Phi_1}^{2\rho \Phi_2} \cos^3 \Phi_z \left( \sin^2 \Phi_z - n_{21}^2 \right)^{-1/2} d\Phi_z dh}{\int_0^{2\rho \Phi_2} \int_{\Phi_1}^{2\rho \Phi_2} \sin \Phi_z \cos \Phi_z d\Phi_z dh} \quad (4.20)
$$

where the integration limits $\Phi_1$ and $\Phi_2$ depend on the surface for which the absorption coefficient is calculated. In contrast to the case of a straight fibre core, there is an additional integration over the fibre diameter to cover all angles and positions at which a ray can enter the bend. Another point that must be taken into account is that since only one surface is considered at a time, the expression must be divided by two, in contrast to the case of a straight sensor probe (equation 4.17). The sum of the absorption at both surfaces then yields the effective absorption coefficient of the bend

$$
\gamma_{\text{eff}} = \gamma_{\text{eff}}(\Phi_1, \Phi_2)_{sf} + \gamma_{\text{eff}}(\delta_1, \delta_2)_{sf} \quad (4.21)
$$

where the respective angles are [179]

$$
\begin{align*}
\phi_1 &= \sin^{-1} \left( \frac{(R + h)n_{cl}}{(R + 2\rho)n_1} \right) \quad (4.22) \\
\phi_2 &= \sin^{-1} \left( \frac{R + h}{R + 2\rho} \right) \quad (4.23) \\
\delta_1 &= \sin^{-1} \left( \frac{(R + h)n_{cl}}{R n_1} \right) \quad (4.24) \\
\delta_2 &= \pi/2 \quad (4.25)
\end{align*}
$$

Again, numerical calculations of the $\gamma/\alpha$ ratio were carried out in Mathcad® and the results were compared with those previously gathered for a straight probe.

Figures 4.7 and 4.8 show bespoke ratio versus the surrounding refractive index for different bend radii of a 100$\mu$m fibre. The other fibre parameters were identical to the straight probe. The only difference in the two figures, again, is the numerical aperture of 0.2 in figure 4.7 and 0.4 in figure 4.8 respectively.

It is clear from both figures that the sensitivity at a constant SRI increases as the bend radius decreases, in addition to the dependencies found for the straight fibre probe. At the same time though, the refractive index range that can be measured decreases with the bend radius. Both effects, the increase in sensitivity and the increasingly confined refractive index measurement range, show a proportional
4.1 Evanescent sensor probe

**Figure 4.7:** Numerical results of the $\gamma/\alpha$ ratio versus SRI at different bend radii ($\rho=100\mu m$, $NA=0.2$, $n_1=1.457$, $n_{cl}=1.433$, $\Phi_c=82^\circ$, $\lambda=633nm$).

**Figure 4.8:** Same as figure 4.7 except for the numerical aperture which is 0.4 in this case ($n_{cl}=1.401$ and $\Phi_c=74^\circ$).
dependence on the numerical aperture of the fibre. A comparison of the absorption coefficients at a fix SRI is given in table 4.1 at the end of this section.

In figures 4.9 and 4.10 the same ratio is shown versus the radius of the bend for different fibre core diameters at an SRI of 1.335 which is approximately the lowest refractive index that must be detected when monitoring aqueous solutions. The graphs also seem to indicate that refractive indices cannot be measured effectively at bent radii below a certain value. In reality the sensitivity actually starts to drop when

![Figure 4.9](image1)

**Figure 4.9:** $\gamma/\alpha$ ratio versus bend radius for different fibre core radii at an SRI of 1.335 and an NA of 0.2.

![Figure 4.10](image2)

**Figure 4.10:** Same as figure 4.9 except for the numerical aperture which is 0.4.
the bend radius becomes even smaller but that effect is not covered by the presented theoretical approach. With that in mind it is clear that there is an optimal bend radius which is the smaller the thinner the fibre core is and the smaller the lowest refractive index to be measured (the latter relationship is not shown in the graphs).

The plots verify the above findings but also show that at a certain bend radii the sensitivity of a larger fibre core can be greater than that of a fibre with a smaller diameter (more so for lower NA values), a phenomenon that was also experimentally observed in [185].

However, the theoretical values of radii that correspond to the maximum sensitivity for each fibre core diameter seem to be larger than experimentally observed values. Khijwania, for instance, found the optimum radius of a 600\,µm fibre to be approx. 1.2\,mm and that of a 200\,µm fibre to be even smaller than 1\,mm [185]. The results were obtained with U-shaped sensors exposed to cobalt chloride dissolved in isopropanol. According to the simulation results, SRIs around water cannot be sensed using bend radii smaller than 3\,mm so there is a discrepancy between the theoretical results and the empirical values.

It also must be noted that while the results obtained for the straight probe match with the values published by Gupta and coworkers, those of the bend shape do not match [179]. The reported absorption ratios for the different bend radii are about twice as large as the calculated values. Since the authors did not mention what software or method they used it was not possible to reproduce the published values by the time of submission of this thesis so that a reason for the deviations cannot be given.

4.1.5 Multiple bends, meander probe

In this section a meander-shaped sensor probe consisting of multiple bends in opposite directions is considered. The first bend of such a geometrical structure is to be treated as described in the previous section. A different approach, though, must be employed to quantify the evanescent absorption of the other bends because the range of incident rays at the second bend, for instance, is differs from the situation at the entry point of the first bend. For clarification, figure 4.11 shows the different types of rays that propagate on a bend fibre core.

Besides the refracting and whispering-gallery rays which contribute to the evanescent absorption, there is a third type of rays on a bend that must be accounted for: tunneling rays. In the straight portion of the fibre those rays undergo total internal reflection at large angles, with respect to the core/medium interface. At the entry point into the bend, i.e., their first reflection at the curved core boundary, those an-
angles are transformed into much smaller ones which causes a great amount of a ray’s intensity to be refracted to the outside of the core. This radiation loss can actually be observed with the naked eye as a bright spot at the outer bend surface when using a visible light source (marked area around the refraction of the tunneling ray in figure 4.11).

As a result, those rays do not contribute to the overall intensity at the exit of the bend because even if a small amount of light is reflected into the core from the entry point, it will certainly be lost after further consecutive reflections along the bend due to the small incident angles. The angles of the refracting and whispering-gallery rays that do exit the bend, however, are transformed back into their original angles (in an ideal U-bend design) on their transition from the bend into the straight fibre portion after the bend. The situation in the following straight fibre section is now different to that in the straight part that leads to the first bend because there are no rays present anymore that are reflected at large angles. The latter conclusion is of major importance because it means that all consecutive bends are “virtually” illuminated under a selective ray launching condition which makes them more sensitive than the first bend.

The overall sensitivity of a structure that comprises \( n \) consecutive U-bends is hence more sensitive than \( n \) U-bends treated separately. The effect increases as the bend radius and fibre core diameter decrease. The reason for that is that the smaller the bend radius the smaller the angle of incidence of an arbitrary ray at the entry point into the bend. Consequently, more rays will be transformed into tunneling rays so that the range of incident angles of the remaining guided rays in the following straight fibre section becomes smaller. Those remaining angles are consequently the ones closest to the critical angle.

In order to use the theoretical approach of the previous sections for the quantification of the described phenomena, the angles that represent the upper integration limits must be addressed. In the case of the bends that follow after the first one, those angles no longer stand for the maximum incident angles at the respective surfaces.

**Figure 4.11**: Rays on a bend fibre core. Tunneling rays account for radiation loss at the entry point into a bend.
(e.g. 90° at the inner surface) because rays at such large angles are not present in the fibre anymore. Therefore, the upper integration limits are just a few degrees larger than the lower integration limits and are dependent on the geometrical dimensions of the first bend and the fibre parameters.

A comprehensive analytical description that includes all the involved parameters would be beyond the scope of this investigation but the effect is illustrated by limiting the upper integration angles in equation 4.20 to be 3° greater than the lower limits which simulates a selective ray launching condition for a U-bend.

In figure 4.12 and 4.13 the γ/α ratios per unit length of a straight probe, a U-bend probe and a meander probe consisting of three U-bends of which the two latter bends were simulated under the mentioned limited integration angle condition, are compared for two different NA values.

![Graph](image.png)

**Figure 4.12:** Comparison of the γ/α ratios of a straight sensor probe, a bend probe and a meander-shaped probe versus the SRI under the conditions addressed in the text. The bend radius of the respective probes is 5mm, the fibre radius is 100µm for each of the cases and the numerical aperture of the fibres is 0.2.

The fibre parameters were chosen in accordance to the previous simulations and the bend radius was set to 5mm. In the case of the fibre with an NA of 0.2 the sensitivity of the meander probe is only slightly greater than that of three separate U-bend sensors but increases with increasing NA. The measurable SRI range decreases in a similar manner as mentioned before when the single bend sensor probes where evaluated in section 4.1.

The qualitative numerical results match with the expected behaviour but the quantitative values might differ from real as pointed out in the previous sections. In practice, i.e., in the case of non-ideal U-bends, there are still tunneling rays in the bends...
that follow the first one but their number is greatly reduced, appearing as a very low intensity spot at the entry point of the second turn, for instance.

However, in the results chapter it will be shown that the sensitivity of a meander sensor at a very small bend radius (approx. 1mm) is dramatically greater than that of a single U-bend sensor.

A point that was not considered in the sections above, apart from the skewness of rays, is the influence of the refraction or radiation loss at the entry point into a bend on the sensitivity as it is not only the evanescent absorption that causes a drop in the light intensity that is acquired at the end of a fibre sensor.

4.1.6 Summary

It was shown that an evanescent absorption coefficient can be analytically described on the basis of a Fresnel power transmission coefficient even though the latter does not incorporate the influence of skew rays which is why the numerical results are overestimations of the real case. However, the method is frequently used until today [199].

The qualitative dependencies of the fibre parameters and surrounding conditions on the sensitivity can be summarised as follows: The sensitivity of an evanescent fibre-optic sensor increases

(i) as the fibre core radius decreases,
(ii) as the numerical aperture increases,
(iii) under selective ray launching condition,  
(iv) as the surrounding refractive index increases,  
(v) as the bend radius decreases (down to a certain value),  
(vi) with the length of the unclad region, and  
(vii) with an increase in skewness.

Another important aspect is the measurable refractive index range which decreases with the bend radius and with an increasing NA.

In table 4.1 the gains in sensitivity at an SRI of 1.335 and a fibre core diameter of 100\(\mu\)m are summarised for the discussed sensor shapes. Simulation results are listed for both collimated and diffuse illumination at numerical apertures of 0.2 and 0.4, respectively. The intention is to provide a set of reference data for present literature values as well as for new and improvement evanescent absorption prediction methods to quantify their gain in accuracy.
Table 4.1: Numerically derived evanescent absorption coefficients $\gamma$ normalised to the bulk absorption $\alpha$ for different sensor geometries and fibre parameters at a surrounding refractive index of 1.335. The other fixed parameters are: $\lambda=663\text{nm}$, $\rho=100\mu\text{m}$, $n_1=1.457$, $n_{cl}=1.443$ (NA=0.2), $n_{cl}=1.401$ (NA=0.4).

<table>
<thead>
<tr>
<th>Type</th>
<th>Collimated illumination</th>
<th>Diffuse illumination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma/\alpha \times 10^4$</td>
<td>ratio</td>
</tr>
<tr>
<td>Straight</td>
<td>1.05</td>
<td>1.00</td>
</tr>
<tr>
<td>Bend (R=15mm)</td>
<td>1.31*</td>
<td>1.25</td>
</tr>
<tr>
<td>Bend (R=10mm)</td>
<td>1.75*</td>
<td>1.67</td>
</tr>
<tr>
<td>Bend (R=5mm)</td>
<td>3.33*</td>
<td>3.17</td>
</tr>
<tr>
<td>Bend (R=3mm)</td>
<td>6.64</td>
<td>6.32</td>
</tr>
<tr>
<td>Meander* (R=5mm)</td>
<td>10.35</td>
<td>9.86</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>NA=0.4</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Straight</td>
<td>5.19</td>
<td>1.00 (4.94)</td>
<td>4.87</td>
<td>1.00 (4.68)</td>
<td>1.401</td>
</tr>
<tr>
<td>Bend (R=15mm)</td>
<td>5.75*</td>
<td>1.11 (5.48)</td>
<td>5.43</td>
<td>1.11 (5.22)</td>
<td>1.382</td>
</tr>
<tr>
<td>Bend (R=10mm)</td>
<td>6.18*</td>
<td>1.19 (5.89)</td>
<td>5.82</td>
<td>1.19 (5.60)</td>
<td>1.373</td>
</tr>
<tr>
<td>Bend (R=5mm)</td>
<td>8.41*</td>
<td>1.63 (8.01)</td>
<td>7.73</td>
<td>1.59 (7.43)</td>
<td>1.347</td>
</tr>
<tr>
<td>Meander* (3 bends) (R=5mm)</td>
<td>32.47</td>
<td>5.65 (30.92)</td>
<td>30.73</td>
<td>6.31 (29.55)</td>
<td>1.347</td>
</tr>
</tbody>
</table>

* These values differ from the ones published in [179] calculated using the same equations.

* The meanders include 3 bends and the upper integration angle was set as the lower integration angle $+ 3^\circ$. 
4.2 Ringdown fibre-cavity

Ringdown principles are based on absorption spectroscopy where electromagnetic waves are attenuated by passing an absorbing medium. Considering an open path cell the absorption within is described by the law of Beer-Lambert

\[ I = I_0 e^{-\delta l n} \]  

where \( I \) and \( I_0 \) are the intensities of the transmitted and incident light, \( l \) the absorption length, \( \delta \) the absorption cross section, and \( n \) the particle density. Usually the product of the two latter is referred to as the absorption coefficient \( \alpha \) which leads to the most general form of the Beer-Lambert law:

\[ I = I_0 e^{-\alpha l} \]  

There are other forms to be found in literature where the absorption coefficient is expressed in different ways to directly calculate the concentration of a substance or to identify the latter, for instance. However, for the following explanations the general form of equation 4.27 is sufficient. It is clear from the equation that for a given absorption coefficient, i.e., a given substance, the light attenuation only depends on the absorption length. For practical reasons absorption cells in the NIR spectral range rarely extend a length of 30cm which at the same time is the limiting factor regarding the sensitivity of this method. Thus, it is hardly applicable for the determination of trace elements which was the initial point for the development of optical long path cells and ringdown cavities. It was shown in section 3.5 that the former are based on the measurement of the amount of light absorption whilst the latter are based on a more sophisticated rate of absorption measurement which will be discussed in the following.

4.2.1 Intensity decay in a regular ringdown cavity

In this section a generalised discussion of the intensity decay in ringdown cavities is given. The exemplary cavity is considered to be confined by two mirrors \( M_1 \) and \( M_2 \) of typically the same reflectivity \( R \) and spaced at distance \( l \), as shown in figure 4.14. The mirrors thereby represent any kind of reflective element, be it coatings, fibre gratings, optical couplers or others. Furthermore, the treatment is based on a pulsed cavity input signal where the cavity is operated in the time domain which means an acquisition of the intensity decay in a time resolved manner (other methods include resonant cavities for the purpose or quantify the phase shift of an oscillating signal in
the frequency domain). It shall be noted that White-type cells and Herriott-type cells are not considered as ringdown cavities but simply as optical long path cells as they are not based the rate of absorption measurements but on the amount of absorption measurements.

Figure 4.14: Sketch of the optical long path cell principle for rate of absorption measurements.

Assuming, in accordance with figure [4.14], that a pulse of intensity $I_0$ is coupled into the cavity through mirror $M1$, the major amount of its intensity $I_0R$ gets reflected. Just a very small amount of the pulse intensity $I_0(1 - R)$ is transmitted through the mirror and is then attenuated by equation [4.27] when propagating along the cell which is filled with an absorbing medium. In the case of fibre cavities an additional attenuation is incurred by the fibre and the sensor element but to simplify matters all light absorption within the cavity is included in $\alpha$. Consequently, when the pulse strikes the second mirror $M2$ it has an intensity of

$$I = I_0(1 - R)e^{-\alpha l} \quad (4.28)$$

There, its major amount $I_0(1 - R)Re^{-\alpha l}$ is reflected back into the open path cell but a small amount of

$$I = I_0(1 - R)^2e^{-\alpha l} \quad (4.29)$$

leaks out the cavity which can be acquired behind $M2$. Based on that position, after a full round trip through the cavity, which means passing the absorbing medium, reflection at mirror 1, and again passing the absorbing medium, the pulse strikes $M2$ again and an intensity of

$$I = I_0(1 - R)^2R^2e^{-3\alpha l} \quad (4.30)$$
leaks out and another round trip later it will have dropped to

\[ I = I_0 (1 - R)^2 R^4 e^{-5\alpha l} \]  (4.31)

From equations 4.29 to 4.31 a general expression can be derived for the intensity level that can be detected behind each of the mirrors dependent on the number of intra-cavity reflections \( n \):

\[ I_n = I_0 (1 - R)^2 R^{n-1} e^{-n\alpha l} \]  (4.32)

Since the decay rate of the exponentially decaying function is constant, for a given absorption and mirror reflectivity, it is independent from the point the acquisition starts. If the initial intensity (\( I_1 \)) value is regarded as the first pulse intensity that is observed behind mirror 2, then the term \((1 - R)^2 e^{-\alpha l}\) in equation 4.32 can be omitted so that with each additional round trip \( I_1 \) is attenuated by a constant factor of \( R^2 e^{-2\alpha l} \). That reduces equation 4.32 to

\[ I_n = I_1 (R e^{-\alpha l})^{2n^*} \]  (4.33)

where \( n^* \) is the number of round trips. Compared with equation 4.27 the attenuation factor is multiplied by two times the number of round trips which causes a significant increase in sensitivity for a given cavity length. It is also clear from the equation that in order to achieve maximum absorption by maintaining small sensor dimensions at the same time, the key parameters are the reflectivity of the mirrors and the absorption within the cell as they defines the number of round trips.

4.2.2 Intensity decay in the proposed fibre-cavity

As stated in section 3.5.4 the main problem of the above type of ringdown cavities is their great insertion loss by means of the major amount of the input signal being reflected at the first mirror, FBG, coupler or the like. The small amount of light that is coupled into the cavity then faces the same loss when passing the second mirror the detector is located behind. Thus, costly ultra-sensitive detectors and strong light sources are required.

The fibre-cavity used in this investigation is capable of reducing the insertion loss down to normal fibre coupling losses by using a multimode fibre whose end faces are coated with reflective metal film. In contrast to other mirror coating designs, a single-mode fibre is attached to a micro hole in the metal layer so that light can be coupled into the multimode cavity at low loss. More details about the manufacturing
process are given in the experimental and results chapter (section 5.2.1). However, the decaying pulse intensities can be acquired through the same hole using a bi-directional transmitter/receiver module, as shown in figure 4.15, or through a second hole in the coating of the other fibre end face which would implicate an additional loss per round trip though.

Figure 4.15: Principle of operation of the proposed multimode fibre-cavity. Light is launched into the cavity through a micro-hole in one of the metal coated fibre end faces reducing the coupling loss of common fibre-cavity designs.

The operating principle of the multimode cavity design in figure 4.15 is based on the following assumptions. When a transversal single mode is coupled into the multimode fibre, many modes will be excited causing the pulse to broaden in the spatial dimension towards the fibre boundary. In figure 4.16 a simulation of this effect is shown for a 400µm fibre. The software package that was used is Beam Propagation Method (BPM), in version 1.4-3. It can be seen in the figure that, with increasing distance from the coupling point, the intensity gradually decreases in the centre region of the core by energy transfer to adjacent modes. Thus, the intensity distribution broadens in the spatial dimension until it spreads the entire
fibre core after just a few millimeters. If such a spatially broadened pulse now strikes the coating that includes the micro hole then it is clear that just a small portion of the overall intensity leaks out the cavity whilst the much greater portion is reflected by the coating that surrounds the micro-hole. The intensity gap in the central fibre region then disappears again through energy exchange between adjacent modes as the pulse propagates back into the cavity, resulting in the re-establishment of a “uniform” field distribution but with a slightly decreased amplitude.

To describe the detectable intensity decay analytically, the influence of the micro-hole in one of the mirrors on its effective reflectivity must be taken into account, in contrast to the case in the previous section. Assuming a uniform intensity distribution over the entire fibre core radius, the original reflectivity of the coating material $R_1$ can be multiplied by a simple factor $k$ that specifies the drop in reflectivity through a cross sectional relation between the remaining coated cross section and the cross section of the entire fibre core

$$k = \frac{r_{\text{core}}^2 - r_{\text{hole}}^2}{r_{\text{core}}^2}$$  \hspace{1cm} (4.34)

where $r_{\text{core}}$ and $r_{\text{hole}}$ are the radii of the fibre core and the micro-hole, respectively. It is clear from equation 4.34 that $k$ is always smaller than one for any value of $r_{\text{hole}}$ greater than null. Figure 4.17 shows this cross section ratio versus the fibre core diameter for different hole diameters.

![Image](image_url)

**Figure 4.17:** Cross section ratio of the coated cross section after milling (shaded area) and the fibre core cross section versus fibre core diameter for different hole diameters.

It can be seen in the figure that for relatively small core radii the additional loss due to the hole has quite a big impact on the overall end face reflectivity but in the
regarded case of a 400 µm fibre core and a 10 µm hole this additional loss is very low. The hole diameter should be kept as small as possible, dependent on the operating wavelength or mode field diameter of the optical source signal.

By substitution of $R^2$ in equation 4.33 with $kR_1R_2$, the intensity after $n$ round trips in the proposed fibre-cavity is

$$I_n = I_1(kR_1R_2 e^{-2\alpha l})^n$$

or with all the parameters that characterise the cavity being placed in the argument of the decay function it is:

$$I_n = I_1 \exp \left(-n(-\ln(kR_1R_2) + 2\alpha l)\right)$$

(4.36)

In the case of a sensor element being inserted into the fibre-cavity, an additional loss per round trip must be accounted for, defining the sensor’s absorption coefficient and length which, in the case of an evanescent field sensor, can be described by $2\gamma l'$ where $l'$ is the length of the unclad fibre region.

$$I_n = I_1 \exp \left(-n(-\ln(kR_1R_2) + 2\alpha l + 2\gamma l')\right)$$

(4.37)

As mentioned above other ways of the description of those additional losses are feasible, e.g., when splices must be considered or a certain physical quantity of the monitored substance is looked for etc.

### 4.2.3 The decay time constant

Since exponential decays are typical physical phenomena and their determination a common task, there were numerous methods developed to extract the decay time constants of mono and multi-exponential decays from experimental data. Istratov and Vyvenko reviewed the most common methods such as Fourier transform, nonlinear least squares (NLS) analysis, Prony’s method, the method of moments, and others [281]. Out of these, the most practical method with regard to ringdown traces is the Fourier transform because of its independence from baseline offsets and the amplitude of the original laser pulse.
Assuming the transient to be single exponential, it is described by the general form of equation 4.38 [281], characterised by its amplitude $A$, the decay rate $\lambda = 1/\tau$, and a commonly present offset $B$ [281].

$$f(t) = Ae^{-\lambda t} + B = Ae^{-t/\tau} + B$$

(4.38)

Since the quotient of the real and the imaginary component of a Fourier transformed function $f(t) \rightarrow F(\omega)$ yields the argument $\lambda$ or $1/\tau$ of $f(t)$, the decay time can be easily determined for any nonzero angular frequency $\omega$ using a fast Fourier transform (FFT) algorithm [281].

$$\lambda = -\omega \frac{\text{Re}\{F(\omega)\}}{\text{Im}\{F(\omega)\}} = \frac{1}{\tau}$$

(4.39)

In the time domain, $\tau$ can be directly determined from equation 4.37 when substituting the discrete variable $n$ with a continuous time variable $t = 2n\co/c_0$ that describes the pulse propagation time for each round trip, where $n_{\co}$ is the fibre core refractive index and $c_0$ the speed of light in vacuum [282]. That results in a time dependent intensity level of

$$I(t) = I_x \exp\left(-\frac{t}{\tau}\right) \approx I_x \exp\left(-\frac{c_0 t}{2n_{\co}} (-\ln(kR_1R_2) + 2\alpha L)\right)$$

(4.40)

which includes the definition of $\tau$ for the sensor-less fibre-cavity:

$$\tau = \frac{2n_{\co} L}{c_0 (-\ln(kR_1R_2) + 2\alpha l)}$$

(4.41)

Based on that and according to equation 4.37, the decay time constant $\tau_0$ in the case of a present evanescent field sensor may be written as

$$\tau = \frac{2n_{\co} L}{c_0 (-\ln(kR_1R_2) + 2\alpha l + 2\gamma l')}$$

(4.42)

where $L$ is the overall cavity length, $l$ the fibre length excluding the sensor element and $l'$ the length of the latter.

### 4.2.4 Summary

It was shown that the insertion loss of fibre-cavities can be significantly reduced from almost 100% to a normal fibre coupling loss by using the proposed multimode cavity
design. The intensity of a single ground mode is distributed over several modes after entering the cavity of which most of the modes are being reflected by the coated cavity boundaries. The influence of the hole diameter on the reflection loss as well as analytical descriptions for the intensity decay and the decay time constant were worked out.

A major advantage of the proposed cavity design is its ability to be operated with standard low-power laser diodes which results in cost reduction, potential miniaturisation, and improved robustness of the system. On the receiver side, photo diodes with low feedback resistors can replace photo multiplier tubes or detector circuits with huge feedback resistors, improving the system stability.

Finally, there is a great number of potential sensor elements that can be inserted into the cavity, basically all sensors that have been previously used in combination with the multimode fibres such as tiny air gaps, evanescent sensors, micro fluid cells or micro gas cells, for instance. In terms of evanescent field sensors, bent fibres are possibly not perfectly suitable as their attenuation at low bend radii is fairly high so that only very few round trips can be achieved which still would mean an n-fold increase in sensitivity with \( n \) being the number of round trips.
5 Experimental results and discussion

To experimentally prove the concepts of both the novel evanescent field sensor probe and the novel fibre-cavity design, their fabrication processes, used measurement setups and obtained results are described and discussed in this chapter.

Different evanescent field sensor probes, i.e., a U-bend sensor, a coiled fibre sensor of one and a half turns, and a meander-shaped probe, were compared on the basis of their sensitivity to aqueous solutions of acetone, ethanol, methanol, 1-propanol and 2-propanol. Broadband measurements in the visible spectral range are carried out to determine the wavelength(s) of maximum sensor response. The findings were then used to characterise the sensors at that wavelength using a low cost LED and photodiode based hardware setup. Finally, the influence of the fibre core diameter at a fixed bend radius on the sensitivity was investigated.

The focus with regard to the ringdown fibre-cavity is on the manufacturing process and the experimental proof of principle. The challenges that occurred during fabrication are addressed as well as the decisive operating parameters. The ringdown trace of the investigated cavity is shown and different ways to improve its response with respect to the ringdown time (decay time constant) are discussed.

5.1 Evanescent field sensor probe

In this section it will be shown that simple U-bend sensors have very limited sensitivity with regard to small refractive index changes in the 1.33-1.34RIU range while the investigated meander-shaped sensor geometry allows for the detection of index changes as low as $5 \times 10^{-5}$, using a simple, low cost, LED based measurement setup.

5.1.1 Sensor fabrication

The first bent fibre sensor probes were made from quartz/quartz fibres (AS 600/660 UVSE) with a core diameter of 600$\mu$m and a numerical aperture of 0.22, purchased from fiberware GmbH. A sufficient long part of the coating was removed in an open
flame from the central region of an approximately 50cm long piece of fibre and burned off afterwards to ensure a complete removal of the cladding for an optimal interaction with the surrounding substance. The exposed fibre core was then heated in a propane flame and manually bent to the desired shape. During the bending process care was taken to maintain a low bending force to ensure that the fibre core diameter remains the same throughout the bent region. To investigate the influence of fibre core diameter on the sensitivity of the three sensor shapes, they were fabricated at identical bend radii of about 1.1mm. Bare fibre adapters were used to connect the sensor probes with the optical sources and receivers.

Figure 5.1 shows photographs of the three fabricated sensor probes, a U-bend sensor, a coil-shaped probe of one and a half turns, and a meander-shaped sensor of three consecutive U-bends.

![Figure 5.1](image-url) **Figure 5.1:** Photographs of the three sensor shapes used in this investigation.

Meander-shaped sensors were also fabricated using 600µm, 400µm and 200µm plast clad silica (PCS) fibres (NA=0.4) which are compared on their sensitivity in section 5.1.3. In this case the fibre ends were glued into SMA connectors and flat polished afterwards to lower the insertion loss of the sensors and to facilitate inserting different sensors into the optical link between the source and the receiver at reproducible conditions.

It shall be noted that U-bends can be easily manufactured at smaller bend radii but in the case of meander shapes previous bends tend to deform while further bends are added when using an open flame. This limitation can probably be overcome by using a laser as heat source because of the absence of a heat cone that affects adjacent bends.

### 5.1.2 Measurement setup

To characterise the different sensor probes, two different measurement setups were used. Broadband measurements were carried out in the visible wavelength region to
determine the wavelength at which the sensor response peaks. The visible spectral range was chosen because appropriate LEDs are available at very low cost. Measurements at a single wavelength were then performed using a micro controller based hardware setup. A simplified functional block diagram of both setups used in this investigation is shown in figure 5.2.

Figure 5.2: Simplified functional block diagram of the two measurements setups used for the evaluation of the sensor probes.

The broadband setup comprised a deuterium-halogen lamp (DH-2000-FHSA-DUV, Micropack) and an Ocean Optics spectrometer module (SR2000-TR) which was connected to a PC via its integrated ADC1000-USB interface. Spectra between 450nm and 700nm were acquired and stored into files once a second using a LabVIEW® program.

For the measurements at a single wavelength, a low cost device was developed whose functionality is explained with reference to figure 5.3. The optical source is a simple LED whose output power is split and injected into two different fibres of which one is connected with the sensor element and the other one with a reference channel which allows for the determination of source intensity drifts. In the figure the splitting
part is represented by an optical coupler which was initially used but later replaced by two optical fibres which were directly glued to the flat polished LED housing. Both the receiver and the reference channel are identically designed. Each consists of a UV enhanced silicon photodiode (UVS-025), an I-to-V stage (OPA381), a digitally controlled voltage amplification circuit (PGA205) and an offset reduction stage which is integrated in the PGA. A microcontroller (MSP430F169) that sits in the centre of the whole application samples the two channels, sets hardware parameters and transmits the acquired measurement data to a PC where it is displayed and stored by another LabVIEW® program. The offset reduction voltage level is independently provided for the two channels by the two DACs (digital to analog converters) that are included in the microcontroller.

In case of the broadband measurements, the sensors were connected to the source and the receiver device using 600µm plastic optical fibres (POF), in connection with the previously mentioned bare fibre adapters. For the measurements at a single wavelength, the POFs were replaced by PCS fibres of core diameters that matched with those of the different sensor probes to reduce losses on the optical link due to different core diameters and refractive indices. In both cases the sensor elements were exposed to the fluids in an appropriate glass container and the measurements were carried out in a dark room at around 20°C. Figure 5.4 shows a joint photograph of both setups used in this investigation.

Figure 5.4: Photograph of the measurement setups used in this investigation.
5.1.3 Results and discussion

Before discussing the sensor responses, the refractive indices of the fluids used in this investigation must be addressed. Figure 5.5 shows the indices of all five fluids diluted in water over the entire solute concentration range at a wavelength of 589nm and a temperature of 20°C.

![Figure 5.5: Refractive indices of acetone, ethanol, methanol, 1-propanol and 2-propanol in water versus the entire solute concentration range at 589nm and 20°C.](image)

The graphs are multi-polynomial fits of the literature data.

It is clear from the figure that the relationship between the refractive index and the solute concentration of each fluid is non-linear. In the cases of acetone, ethanol and methanol there is even a turning point where the initially increasing refractive index starts to decrease again at a certain point as the solute concentration further increases which makes high resolution concentration measurements impossible around those turning points. In the lower concentration range, however, a monotonically increasing, almost linear relationship between both quantities can be observed for each fluid (figure 5.6) which makes concentration monitoring based on refractive index acquisition perfectly possible in that range.

The concentration range that can be covered by this measurement technique depends on the respective fluid though. In the case of the two n-propanols the whole concentration range up to 100% can be covered but the change in the refractive index $\Delta n$ decreases as the propanol concentration increases which supposedly causes a decrease in sensitivity. On the other hand, the evanescent absorption was shown to increase with the refractive index of the surrounding medium (section 4.1) so that decrease in $\Delta n$ can be compensated to some extent.
Figure 5.6: Same as figure 5.5 except for the concentration range which is 0-10% wt. The symbols represent the literature values while the line graphs are linear fits of the latter.

However, the focus in this investigation is on the lower concentration range of 0-10% wt. The average index change per integer concentration step of each fluid is listed in table 5.1. The given ratios are the multiples of the methanol case and are later used to evaluate the sensor responses. It is clear from the numbers listed in the table that the sensor resolution must be in the $10^{-5}$ RIU range to resolve concentration changes $\ll 1$% wt for the investigated fluids.

<table>
<thead>
<tr>
<th></th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Acetone</th>
<th>2-Propanol</th>
<th>1-Propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta n \times 10^4$</td>
<td>2.3</td>
<td>6.4</td>
<td>7.1</td>
<td>9.0</td>
<td>9.3</td>
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<td>ratio</td>
<td>1.0</td>
<td>2.8</td>
<td>3.1</td>
<td>3.9</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Generally, the refractive index of a fluid is known to vary with temperature, wavelength and pressure. Assuming that, during an experiment, the source wavelength does not vary significantly over time and so does the pressure, the remaining influence that can affect the measurement resolution is the temperature, a very common challenge in the area of sensor calibration. The temperature coefficients of the refractive indices $\Delta n/\Delta T$ of the five fluids were reported in numerous publications. In table 5.2 typical values found in literature are summarised.

Out of the coefficients given in the table, the drifts mainly referred to are: $-5.0 \times 10^{-4}$/°C (acetone), $-3.9 \times 10^{-4}$/°C (ethanol, methanol, propanol), and $-1.0 \times 10^{-4}$/°C (water). With these values known, temperature drifts can be corrected for by proper
Table 5.2: Temperature coefficients of the refractive indices $\Delta n/\Delta T$ of the fluids used in this work.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$-\Delta n/\Delta T \times 10^{-4}$/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>4.9 [283], 5.0 [284]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.6 [283], 3.9 [284], 4.38 [286, 287], 4.53 [286, 288]</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.9 [283, 286, 289], 4.32 [286, 288]</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>3.8 [283], 3.9 [285, 286, 288], 4.33 [286, 288]</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>3.4 [290], 4.63 [288]</td>
</tr>
<tr>
<td>Water</td>
<td>0.8 [285, 286], 0.99 [291], 1.04 [283, 286]</td>
</tr>
</tbody>
</table>

Sensor calibration. Since these values refer to the pure components, they must be weighted according to the compound concentrations of the aqueous mixtures using

$$\frac{\Delta n}{\Delta T} = x_1 \frac{\Delta n_1}{\Delta T} + x_2 \frac{\Delta n_2}{\Delta T}$$

where $x_i$ is the weight fraction of compound $i$ and $\Delta n_i/\Delta T$ the temperature coefficient of the index of refraction of the pure component $i$ of the mixture. This method is intended to be used when the sensor is calibrated for a single temperature and the fluid temperature is continuously monitored when the sensor is deployed.

A more accurate way to correct temperature drifts is a direct determination of a mixture’s refractive index at different temperatures and compound concentrations and to develop an appropriate calibration algorithm. Openhaim and Grushka, for instance, published appropriate results for aqueous methanol mixtures [292]. Such measurements are quite extensive though and result in a fitting equation of two dependent variables.

However, a calibration against temperature is beyond the scope of this investigation. Above remarks were included with regard to future works on the topic.

As mentioned previously, the refractive index graphs shown in figures 5.5 and 5.6 correspond to a wavelength of 589nm. However, experiments are later carried out at 650nm where those refractive indices have slightly different values. The chromatic dispersion $\Delta n/\Delta \lambda$, which describes the refractive index shift versus wavelength, and the respective dispersion formula $n(\lambda)$ of some of the fluids used in this investigation can be found on the refractive index info website[^1]. In the context of this work, however, those shifts are neglected and the ratios given in table 5.1 are used to evaluate the sensor responses.

[^1]: [http://refractiveindex.info](http://refractiveindex.info)
Broadband measurements

The broadband measurements were carried out with the three sensor probes made from quartz/quartz fibres with an NA of 0.22, a core diameter of 600µm and bend radii of approx. 1.1mm [5.1]. The sensors were tested on aqueous ethanol and methanol solutions with alcohol concentrations between 0 and 10%vol, stepwise increased by 1%vol. For each measurement cycle, the first acquired spectrum at 0% solute content (pure water) was used as the reference spectrum. The corresponding relative spectra where then calculated as the quotients of the reference spectrum and the subsequent spectra at varying fluid concentrations so that an increased absorption (decreasing transmitted optical power) would result in a positive change in the relative spectrum.

In the case of the U-bend and coiled-shape sensor probe, no intensity changes could be resolved with the spectrometer over the investigated concentration range whilst the meander-shaped probe did show an increase in the relative spectrum of about 0.27% and 0.78% per concentration step methanol and ethanol, respectively, which was almost constant over the entire inspected wavelength range as shown in figures 5.7 (methanol) and 5.8 (ethanol). The ratio of the values for ethanol and methanol (0.78/0.27=2.9) matches the ratio of their respective refractive index changes per integer concentration step (2.8).

![Figure 5.7](image)

**Figure 5.7:** Relative spectra of a meander-shaped sensor probe versus wavelength for a methanol concentration range of 0-10%vol in steps of 1%vol. The sensor parameters are: fibre core diameter = 600µm, NA = 0.22, bend radius = 1.1mm.

A qualitative evaluation of the graphs in figure 5.8 shows slightly decreasing relative spectra below 500nm as the ethanol concentration increases. The same is true for the central region around 575nm. For those reasons the wavelength to be used for the single wavelength measurements was chosen to be 650nm.
Measurements at a single wavelength

To verify the findings of the broadband measurements, i.e., the meander sensor being more sensitive than the other probes, the same three sensors were tested on the same fluids at 650nm, with the setup described in section 5.1.2. The alcohol concentration was changed every two minutes in steps 1%wt over a range of 0-10%wt. The resulting graphs are shown in figure 5.9 for the case of methanol and in figure 5.10 for the case of ethanol. The graphs also include the fibre parameters and the receiver circuit design (the gain factor of the voltage amplification stage was set to one so only the I-to-V stage is shown).

In the figures, the upper x-axes show the alcohol concentrations for the respective periods of time (lower x-axes). The y-axes are scaled according to the absolute values of the relative changes in the output voltage of the transimpedance amplifier with 0mV indicating pure water. The relative changes were chosen to evaluate the sensors because each sensor probe has a different attenuation resulting in a different voltage offset at the I-to-V stage output at 0% alcohol content. The output voltage $V_o$ is linearly dependent on the incident optical power $P_{ph}$ at the photodiode and the feedback resistor value $R_f$:

$$V_o = I_{ph}R_f = S P_{ph}R_f$$  

(5.2)

In the equation, $I_{ph}$ is the current that flows through the photodiode which is the product of the incident optical power and the diode’s wavelength dependent responsivity $S$. The latter is typically given in ampere per watt (A/W). It is clear from the
5.1 Evanescent field sensor probe

Figure 5.9: Relative change in the output voltage of the I-to-V stage versus methanol concentration in water (0%-10%vol). The graphs show the responses of the three investigated sensor probes at 650nm and 20°C.

Figure 5.10: Same as figure 5.9 but for aqueous ethanol solutions.
equation that the relative change in the output voltage decreases with the incident optical power (increasing alcohol content $\rightarrow$ increasing SRI $\rightarrow$ increasing absorption $\rightarrow$ decreasing transmitted power) but instead of dealing with negative numbers, the absolute values of those changes are shown in the above figures as well as in all the remaining figures throughout this section.

However, it is verified in figures 5.9 and 5.10 that the meander sensor shows a much stronger response to changes in the alcohol concentration than the U-bend and the coil-shaped sensor. In the corresponding graphs of the two latter probes, it is even difficult to identify the points where the concentrations were changed which makes it difficult to quantify how much more sensitive the meander-sensor is. An estimation, however, is given with regard to the ethanol traces where at least tiny steps can be observed. The absolute changes in the output voltage at 10%vol are 1.2mV for the U-bend, 1.4mV for the coil-shaped probe, and 21.2mV for the meander-shaped probe. Based on those numbers, the meander sensor is approximately 18 times more sensitive than the U-bend sensor, with regard to the given fibre core diameter and bend radius. In section 4.1 it was shown that the sensitivity increases with the SRI but as the investigated refractive index range is very small, no SRI-dependent distinction shall be made in this context. The coil-shaped probe was expected to be about three times as sensitive as the U-bend sensor as its length is three times that of the latter. However, the ratio is much smaller which indicates that the evanescent absorption actually has less impact on the sensitivity than the refraction losses at the entry point into the bend. For that reason, the influence of the turning point losses should be investigated theoretically in future works on the topic.

It must be noted that there is an inconsistency in the relative voltage levels in figures 5.9 and/or 5.10. In the meander sensor graphs, the ratio of the output voltages at 10%wt ethanol and methanol is approx. 1.9 which is way below the expected value of 2.8 from table 5.1. A possible explanation is an increased attenuation caused by the connector pair (bar fibre adapters) between the sensor and the receiver. The sensor ends of all probes that were fabricated from that point on were therefore glued into SMA connectors and the error did not appear again in future measurements with the PCS fibres.

Another point that must be addressed with regard to the figures is the varying step height at some concentration levels in the ethanol graph. While the average step height is roughly 2mV per integer concentration step, there are obviously greater step heights on the transitions from four to five percent ethanol and from nine to ten percent, for instance. The most plausible reason for that is that the alcohol content was increased by adding 1%vol of the solute at a time with a syringe so that sometimes
improper mixing could have occurred. Ideally, each step should have the same height as the refractive index difference between consecutive steps is pretty much constant. The spikes at the transition points are caused by the same reason. Every time, the alcohol concentration was increased it sometimes took a few seconds until the fluids were properly mixed. The sensor response is instant though because any change in the surrounding refractive index immediately causes the transmitted power to drop or to increase dependent on which direction the change takes.

However, having quantified the sensitivity ratios of the different sensor probes, further investigations were carried out with different meander sensors to experimentally evaluate the dependence of the fibre core dimension on the sensitivity. This time PCS fibres with core diameters of 200\(\mu m\), 400\(\mu m\), and 600\(\mu m\) and a numerical aperture of 0.4 were used. The bend radii were roughly identical for each probe (1.1mm) and the measurements were performed in the same way as described above. The resulting graphs are shown in figure 5.11 for the case of methanol and in figure 5.12 for the case of ethanol solutions.

![Graph showing the response of sensor probes versus methanol concentration](image)

**Figure 5.11:** Response of a meander-shaped sensor probe versus methanol concentration for different fibre core diameters at a fix bend radius. The respective parameters are shown in the figure.

In both figures, two aspects are verified that were previously highlighted in the theory part (sections 4.1.4 and 4.1.5): The sensitivity of evanescent field sensors increases as the fibre core diameter decreases but in the case of a bent fibre geometry, a sensor made of a larger fibre core can be more sensitive than a sensor made of a thinner fibre, given that the bend radii of both fibres are identical. The first statement is satisfied by the traces that belong to the 400\(\mu m\) and 600\(\mu m\) probes out of which the smaller one is more sensitive. The second statement is proven by the response graphs
Experimental results and discussion

Figure 5.12: Same as figure 5.11 but for ethanol solutions.

of the 200µm fibres which are more sensitive than the respective 600µm probes but less sensitive than the 400µm probes at the same time. Their sensitivity is, however, expected to exceed that of the 400µm probes at some point for bend radii smaller than 1.1mm.

To verify that the measurements are valid with regard to the surrounding refractive indices, the absolute output voltage changes for each probe at 10%vol methanol and ethanol were compared again by means of the ratio of the ethanol case and the methanol case. The results are shown in table 5.3.

Table 5.3: Output voltage differences $\Delta V$ from figures 5.11 and 5.12 at 10% alcohol content for the different fibre core diameters. The ratios correspond to the values acquired for the ethanol mixtures divided by those of the methanol mixtures. The expected ratio is 2.8.

<table>
<thead>
<tr>
<th>$d_{fibre}$ (µm)</th>
<th>Methanol (mV)</th>
<th>Ethanol (mV)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>13.7</td>
<td>41.3</td>
<td>3.0</td>
</tr>
<tr>
<td>400</td>
<td>26.9</td>
<td>72.2</td>
<td>2.7 (3.0*)</td>
</tr>
<tr>
<td>200</td>
<td>16.3</td>
<td>50.0</td>
<td>3.1</td>
</tr>
</tbody>
</table>

* after drift compensation

Given the expected ratio to be 2.8, it can be concluded that the experimentally observed ratios for the 200µm (3.0) and 600µm (3.1) only slightly exceed the expected value while the ratio that belongs to the 400µm (2.7) probe seems to show the best agreement but if the small upward drift caused by the receiver circuit in the respective methanol graph is removed, the voltage level at 10%vol would be a bit smaller which
means that the real ratio is just about the same as in the case of the two other fibre core diameters. Hence, the ratios are all slightly larger than expected but identical for the three fibre diameters so that the measurements are considered to be valid. The source of the mentioned drift could not be located and did not occur again during subsequent experiments.

With the 400µm meander probe found to be the most sensitive one for the given bend radius, it was used to perform tests on additional fluids, i.e., acetone, 1-propanol, and 2-propanol, out of which acetone shows a similar slope in its refractive index graph as ethanol (figure 5.6). The difference in both values at a concentration of 10%wt is $7 \times 10^{-4}$RIU. In the case of the two n-propanols the index slopes are even narrower with a difference of only $3 \times 10^{-4}$RIU at 10%wt but it was possible to clearly resolve those differences with the mentioned sensor probe as shown in figure 5.13. Again, the measurements were carried out in the same manner as in the above tests and the diagram axes show the same quantities.

![Figure 5.13: Response of a 400µm meander sensor with a bend radius of 1.1mm on the aqueous solutions of acetone, ethanol, methanol, 1-propanol and 2-propanol.](image)

By comparing the graphs in figure 5.13 with the corresponding refractive index graphs in figure 5.6 one can observe that the qualitative sensor response for the different fluid compositions is correct. Methanol causes the lowest output voltage changes as its refractive index slope over the investigated concentration range is the smallest of all fluids while in the case of 1-propanol the slope is larger than that of any other fluid in the graph. The quantitative evaluation, again, is done by comparing the refractive index ratios at 10% solute concentration with the output voltage ratios,
with the values of the methanol solution being the reference. A comparison of all values is given in table 5.4 showing a good agreement between them.

**Table 5.4:** Output voltage differences $\Delta V$ from figure 5.13 at 10% solute concentration. The ratios correspond to the value of methanol. The expected ratios were taken from table 5.1.

<table>
<thead>
<tr>
<th></th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Acetone</th>
<th>2-Propanol</th>
<th>1-Propanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta V$ (mV)</td>
<td>26.9</td>
<td>72.2</td>
<td>80.4</td>
<td>98.2</td>
<td>104.7</td>
</tr>
<tr>
<td>Ratio</td>
<td>1.0</td>
<td>2.7</td>
<td>3.0</td>
<td>3.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Expected ratio</td>
<td>2.8</td>
<td>3.1</td>
<td>3.9</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

With the utilisation of a more sophisticated way to add and mix the fluids during the experiments, a perfect match of the ratios listed in the table is considered possible.

From the results shown in the figures 5.9 to 5.13, the resolution of a 400 $\mu$m (NA=0.4) meander probe consisting of three U-turns at bend radii of approx 1.1mm is estimated to be in the order of $5 \times 10^{-5}$ which corresponds to detection limits of 0.2%vol methanol, 0.075%vol ethanol and acetone, and 0.05% n-propanol. However, there are several possible ways to further increase the sensitivity such as by increasing the value of the feedback resistor of the I-to-V stage, by further decreasing the bend radius, or by adding more bends but instead of further stressing the sensitivity, attention was paid to the more general question of to what extend manually fabricated bends result in identical sensor-to-sensor responses. For this purpose four 600 $\mu$m and three 400 $\mu$m meander sensors were manufactured and tested on aqueous ethanol solutions. The results are shown in figure 5.14 and 5.15 respectively.

In the case of the 600 $\mu$m probes, the quantitative response of each sensor is quite similar whilst some deviation can be observed between the graphs that belong to the different 400 $\mu$m probes. This is because the chosen bend radius can be comfortably fabricated on a 600 $\mu$m fibre by heating it at a single point and bending it in a single move so that the radii of multiple probes are pretty much identical. The “natural” bend radius of a 400 $\mu$m fibre when heated at a single point is smaller than the chosen one so that the fibre must be heated gradually along a certain distance in order to form a bend of the desired radius. That process can obviously not be repeated with the very same accuracy which results in different bend radii within a certain range across multiple probes or even across the bends of the same probe, a fairly small range though but big enough to cause the sensitivity to deviate to some extend. Thus, it is a challenging task to manually fabricate identical meander sensors of the same sensitivity and for that reason the development of a proper bending mechanism is
Figure 5.14: Response of multiple 600µm meander sensors manufactured to have roughly the same bend radius.

Figure 5.15: Same as figure 5.14 but for a fibre core diameter of 400µm.
recommend with regard to future works on the topic. The relative changes in the output voltage when exposed to different fluids should be identical though.

5.1.4 Summary

It was shown that the sensitivity of a meander-shaped sensor consisting of three U-bends is not just three times that of a single U-bend sensor but considerably greater (approx. 17 times for the chosen fibre and bend parameters). It was verified that fibres of a smaller radius can be less sensitive than thicker fibres, at a fix bend radius. The meander geometry was tested on five different liquids at varying concentrations and a good agreement between the expected and the experimentally gathered values was achieved.

Different ways of how to further increase the sensitivity of the sensor used in this investigation were proposed such as a larger feedback resistor in the receiver circuit, smaller bend radii and/or more bends. With respect to the manual manufacturing process, it was shown that deviations in the response of multiple “identical” sensor probes are pretty much inevitable and should be addressed in future works on the topic. At the same time, a proper mixing process as well as a more accurate way to change the solvent concentrations should be taken into account to avoid response peaks upon concentration changes and variations in the step heights.

Despite those issues that accompanied the preliminary experiments, the decisive properties of the proposed sensor design are its high sensitivity, small dimensions, low cost and applicability over a wide wavelength range. Besides that, the sensor can be applied to any fluid whose refractive index varies with its compound concentration and whose refractive index is below that of the original cladding. However, the range of detectable refractive indices could be even extended by coating the bent fibre core with appropriate materials, as reviewed in chapter 3.4.4.

5.2 Ringdown fibre-cavity

Based on the fibre-cavity design described in section 4.2.2, the focus in this section is on the design considerations, the fabrication process and the proof of principle.

A quantity that was not addressed in the theory chapter but must be considered when choosing the pulse length with regard to the cavity length is the transit time of a ray on an optical fibre. It is clear that rays of different launching angles have different propagation times with respect to a fix fibre length because rays that propagate in parallel to the fibre axis follow a shorter path along the core than rays that are continuously reflected at the core/cladding interface. The maximum transit time
5.2 Ringdown fibre-cavity

$t_{\text{max}}$ of a ray to cover a distance $z$ on a step index multimode fibre can be written as (equation (3-1) in [171])

$$t_{\text{max}} = \frac{z \cdot n_{co}^2}{c_0 \cdot n_{cl}} \quad (5.3)$$

where $c_0$ is the free-space speed of light and $n_{co}$ and $n_{cl}$ are the refractive indices of the fibre core and its cladding, respectively. In case of the PCS fibre used in this investigation, the core refractive index is 1.457 and that of the cladding is 1.401 (NA=0.4) which results in a maximum ray transit time of approx. 5ns per meter. Along an exposed area of the fibre core, that time increases to about 5.3ns/m for the case of water as the surrounding medium ($n_{cl} = 1.333$). Since the sensor length is commonly much shorter than one meter, the increased transit time due to the surrounding medium can be neglected and a value of $t_{\text{max}} = 5\text{ns/m}$ can be assumed for the entire length of the cavity.

To avoid any superposition or erasement phenomena, the pulse should be much shorter than the cavity. The same is true with regard to temporal pulse broadening due to dispersion of any kind. Hence, with the maximum transit time of the chosen fibre known, the cavity length can be chosen accordingly.

5.2.1 Cavity fabrication process

In section 4.2.2 the novel cavity design was described as a step index multimode fibre bound by metallic coatings on each of the fibre end faces. One of the coatings includes a micro hole through which light can be injected into the cavity at minimum losses.

The coating material was chosen to be gold because it is non-corrosive and thus must not be protected from changing environmental conditions. It also shows high reflectivity over a wide wavelength range (figure 3.24). The gold films were sputter coated onto fibre ends of a 400µm step index PCS fibre. According to Miller and co-workers, the maximum reflectivity of a gold layer in the near-infrared region is reached at a thickness of about 25nm [293]. In another source a value of about 80nm is reported but without referring to the respective wavelength (unfortunately the reference went missing). However, in order to ensure maximum reflection, the layer thickness was chosen to be in the range of 100-120nm.

The challenge in this context was on the fabrication of the micro hole in the coating layer at a reproducible accuracy. Different methods were considered for the purpose. Early investigations comprised spherical fibre ends which where produced by heating the fibre ends until they became round shaped. They were then sputter coated before a small cross section of the fibre tip was plane polished so that a part of the metal layer was removed. Unfortunately, the resulting diameter of the hole in the metal
film was in the 100µm range, even with very little polishing (a few millimeters) and very smooth polishing paper (0.3 micron). Figure 5.16 shows a one of the fabricated spherical fibre tips with a plane polished hole in the coating. Since the purpose is to attach a single mode fibre to the hole, the achieved hole dimension was far too large. For that reason and because of concerns regarding the reproducibility the method was rejected.

![Figure 5.16: Spherical tip of a 400µm optical waveguide, coated with thin layer of gold (left). The fibre tip was plane polished to produce a micro hole in the coating (right) but the resulting hole diameter exceeded the aimed 10µm by a factor of 10.](image)

Other methods that were considered suitable comprised reflective foils attached to the fibre ends, laser drilling and lithography. Reflective foils turned out to be very difficult to handle at such small dimensions. Creases were a major issue as well the exact positioning of the hole, jabbed through the foil with a micro pipette, on the fibre axis. Several companies were contacted for the purpose of laser drilling but the method turned out to be quite costly for prototyping. Lithography is a very reliable and highly reproducible technology that is often used for the creation of micro structures. A company that was contacted offered to produce prototypes free of charge but the time to set up the appropriate devices for the purpose, without interrupting the regular businesses, would have taken about four to five months so that in the end this method was rejected as well.

Eventually, a process called focused ion beam milling (FIB) was employed. Its working principle is comparable to that of electron microscopy with the electron beam being replaced by an ion beam which allows for the ablation of materials down to a nano scale but can also be used for surface imaging. To facilitate the attachment of a single mode fibre to the micro hole that was to be milled, the fibre ends of a 20m long piece of a 400µm 3M™ PCS fibre (NA=0.4) were glued into SMA 905 (sub miniature A) connectors, flat polished with 0.3 micron polishing paper and cleaned in an alcohol solution before the fibre ends were sputter coated with a gold layer. The stainless steel ferrules of standard SMA 905 connectors (128µm) were drilled out
to the desired diameter beforehand using printed circuit board drill bits. A hole of 10µm in diameter was then milled into the coating using an FEI FIB 200 workstation and the following milling parameters: 50nm beam diameter, 50% overlap, 1ms dwell time (the time the ion beam remains at a single location), and about 3min milling time. Figures 5.17(a) through 5.17(c) show different images of milled fibre end faces addressing the main problems that arose throughout the process such as scratched fibre tip surfaces due to imperfect polishing, destroyed coatings due to improper handling of the fibre tips after the coating process, and contaminated coatings due to insufficient cleaning. In figure 5.17(d) a properly coated and milled fibre tip is shown.

(a) Badly polished fibre end face.  
(b) Destroyed coating.  
(c) Contaminated coating due to insufficient cleaning.  
(d) Properly polished, cleaned, coated and milled fibre end face.

**Figure 5.17:** Selection of coated and milled fibre end faces that represent the range of problems that arose during the manufacturing process.

which was used for the experimental investigations in section 5.2.3. The differently shaded square around the hole resulted from an image that was previously taken of
that area as taking images with an ion beam always causes a very thin layer of the material to be removed (milled).

The milling process is highly reproducible with respect to the hole placement and its diameter. Additionally, the fibre end surfaces can be visually inspected before, during and after the milling so that a possibly damaged surface can be detected easily. Finally, a real time visual feedback, provided by the FIB 200 software during the milling process, allows for the determination of the point of time when the ion beam reaches the silica fibre core which can be used as an indicator for the coating thickness. This way fibres with coatings of insufficient thickness, due to a corrupted coating process for instance, can be identified and rejected.

5.2.2 Measurement setup

Initial proof of principle measurements were performed using an optical time domain reflectometer (OTDR). Due to microscopic variations in the density and thus the refractive index along a fibre core, optical energy is continuously lost through scattering in all directions (Rayleigh scattering). An OTDR injects optical pulses into an optical fibre and monitors the back-scattered intensity over time which is transformed into a distance dependent attenuation plot. This way losses along a fibre link, e.g. due to splices, connectors or bends, can be identified and localised. Besides such intensity drops, reflection peaks can be present in OTDR traces which occur at points of refractive index mismatches such as fibre/air gaps between connector pairs, fibre cracks or simply at the fibre end. Figure 5.18 shows an exemplary OTDR trace that includes typical attenuation and reflection events.

It is clear from the figure that connector pairs cause a reflection peak as well as a drop in intensity. Fibre cracks have the same pattern but usually cause a more significant intensity drop. Fusion splices typically do not cause reflection peaks but are represented by a sudden drop in the back-scattered optical power. The first event in any OTDR trace is the reflection peak of the connector that joins the device with fibre to be monitored. Commonly a dummy fibre of some 20-50m in length is inserted between an OTDR and the fibre under test to ensure a so called steady state condition at the entry point into the monitored fibre which basically means a uniform energy distribution over all modes. However, OTDR traces typically end with a strong reflection peak caused by a fibre-to-air interface. Knowing the patterns of different events, losses on a fibre link can be characterised, quantified and localised using an OTDR.

Under certain circumstances so called ghost features can be present in an OTDR trace which must be accounted for in the context of this investigation. If there is a
strong enough reflection at some location on the fibre link then it can cause multiple reflections between the launching point of the fibre and the point of reflection which then appear as additional peaks in the attenuation trace at multiples of the distance of their initial occurrence. In contrast to the reflection feature of a connector pair, ghost do not cause a drop in power and can thus be identified by this criterion.

To avoid such ghosts to be mistaken as or overlaid with cavity reflections, a single mode dummy fibre (Corning SMF-28) of 1km in length was inserted between the OTDR output and the fibre-cavity so that there could not be any ghosts present in the trace for at least another kilometer.

The OTDR used for the experiment was an EXFO IQ-7000 which emits pulses at a wavelength of 850nm, a wavelength at which the reflectivity of gold approaches a value of close to one (figure 3.24). The pulse length was set to be 10ns which corresponds to a spacial dimension of about 2m (equation 5.3) or 1/10 of the cavity length so it was assured that there would not be any disturbing superposition effects due to temporal pulse broadening.

### 5.2.3 Results and discussion

The OTDR trace that was acquired with the the experimental setup described in the previous section is shown in figure 5.19. The overall physical fibre length was 1030m (1010m of dummy fibre and the 20m long cavity).

In the figure, the initial reflection peak of the launching point at 0m distance is followed by a gradual decrease in the back-scattered optical power over the length
5 Experimental results and discussion

Figure 5.19: Entire OTDR trace of the dummy fibre and the fibre-cavity.

of the dummy fibre. The intensity drop caused by the dummy fibre is approx. 3dB which is about 1dB more than advertised by the manufacturer but that has no impact on the experiment. The end of the dummy fibre is marked by a quite intense reflection peak as it is typical for silica/air transitions. In fact, there is a tiny air gap between the end of the dummy fibre and the cavity due to the milled micro hole. Additionally, the physical contact between both connectors was not as tight as possible to protect the coating from being destroyed. The insertion loss of the cavity is about 4dB which could be reduced by covering the coating with a protective layer so that tight physical contact between both fibres is possible without damaging the reflective metal layer. The decaying pulse peaks between 1km and 1.25km prove that once the pulse entered the cavity, it was repeatedly back and forth reflected, just as anticipated. The intensity levels of the first few reflection peaks exceed that of the dummy fibre because it is not just the back-scattered intensity that is detected at the OTDR input but also part the optical power that is reflected at the end of the cavity. Unexpectedly though, the pulses do not fade out to noise level but are overlaid with, as it is believed, an entire ghost trace of the dummy fibre (same length and same slope). It is therefore also believed that additional pulses are hidden below the offset.

A close up view of the decaying pulses is shown in figure 5.20 including the fibre parameters, coating properties and the selected pulse parameters. The loss in optical power per round trip is approximately 1dB of which 0.68dB are due to the fibre attenuation ($\approx 17$dB/km) and 0.32dB are the summarised reflection and micro hole losses. It is clear that a shorter fibre would result in a lower loss per round trip as would a transition of the operating wavelength towards the minimum fibre attenuation of approx. 9dB/km at about 800nm. Hence, using a 10m long cavity operated at 800nm could bring the round trip loss down to half of the observed value.
However, as per equation \[1.33\] the sensitivity of an evanescent sensor probe inserted into a fibre-cavity increases by a factor of two times the number of round trips which makes sense as the light passes the sensor element twice per round trip. In the depicted case, about 17 round trips can be identified which corresponds to an increase in sensitivity of up to 34 times for a sensor element that causes only little additional loss such as a straight fibre probe. Tapers, bent fibres and air gaps have a higher insertion loss which would reduce the number of round trips. However, their sensitivity would still be increased by a factor of the reduced number of round trips.

The dynamic range covered by the decaying pulses in figure 5.19 is quite small, just above 10dB, which is caused by mainly two reasons. On the one hand, the optical power coupled into the dummy fibre is relatively low (-20dBm) which is due to the transition from a 50µm fibre at the OTDR output to the 8.2µm core of the dummy fibre. The other effect that is limiting the dynamic range is obviously the offset of the dummy fibre ghost but even if it was not there, the detection limit of the OTDR (-35dBm) is way above that of common photodiode detectors which can easily resolve intensity levels down to -45dBm or even lower. It is therefore feasible to at least triple the number of round trips by directly coupling light from a single mode laser diode source into the dummy fibre and by detecting the reflected pulses with a custom photo-receiver at the same time. Together with the previously mentioned possibilities of reducing the round trip loss through a shorter cavity length and wavelength transition, these preliminary results are very promising.

Since the decay time constant of a cavity is the quantity of major interest, the pulse peaks in figure 5.20 were fitted to a single exponential function (figure 5.21) whose
decay time was determined to be 0.93\,\mu s. That value corresponds to the “empty” fibre-cavity. It must be re-determined when a sensor probe is inserted into the cavity which then represents its maximum ringdown time. The ratio of the latter and the ringdown time in the presence of an absorbing medium is then a measure for the compound concentration in a liquid solution the sensor is exposed to, for instance.

![Figure 5.21: Determination of the ringdown time through an exponential fit of the decaying pulse peaks.](image)

However, further investigations with a more sophisticated measurement setup and in combination with an evanescent sensor probe (see end of section 3.5.3) are beyond the time frame of this investigation. The focus in this investigation was on the fabrication of the novel type of fibre-cavity and its proof of principle which offer great potential for future works on the topic.

### 5.2.4 Summary

The working principle of the proposed fibre-cavity was experimentally verified which enables fibre-based sensors to be operated in a ringdown scheme at low insertion loss, a major advantage compared to common passive cavity designs. As a result, the cost and complexity of ringdown sensor applications can be greatly reduced because standard laser diodes and photo receivers can be used. The fabrication method was shown to be reliable and highly reproducible. Common metals such as gold, silver and aluminum show high reflectivity in the near infrared wavelength region which makes the cavity applicable for a variety of applications over a wide wavelength range which can even be extended to the visible wavelength range by using specifically designed dielectric coatings.
two ADCs are phase shifted by 180 degrees so that one of them is sampling at the rising edge of the original clock signal and the other one on its falling edge, resulting in an effective sampling frequency of 332MHz (3.3ns). The data transfer from the ADCs to the FIFOs can be easily triggered by the *clock out* signal of each of the ADCs.
6 Conclusions and future work

In this investigation, a fundamental study of an optical fibre sensor capable of monitoring liquid mixtures was carried out. Conventional sensor systems were reviewed and found to have limiting factors in terms of real-time operation at high sensitivity while maintaining low manufacturing cost and long term stability as required for the determination of the alcohol concentration in the liquid feed of different types of direct liquid feed fuel cells, for instance. The ever increasing demand for a sensor configuration that satisfies all the requirements was proposed based on the combination of two optical sensing techniques, i.e., evanescent wave field spectroscopy and ringdown spectroscopy, the latter for the purpose to further increase the sensitivity and long-term stability. In the following section, the conclusions on the development of both the sensor probe and the fibre-cavity are summarised.

6.1 Conclusions

The design, development and experimental evaluation a novel evanescent field sensor probe and a fibre-cavity were described.

As for the sensor probe, a tiny structure consisting of a meander-shaped multimode fiber was found to significantly increase the sensitivity of common evanescent-field sensors. The operating wavelength was chosen to be in the visible wavelength region, at 650nm, as very cheap optical sources and receivers are widely available. However, it was also shown that a wide range of wavelengths is applicable, mainly restricted by the operating wavelength range of fibre type that is used.

Different sensor shapes were compared regarding their sensitivity on five aqueous solutions containing acetone, ethanol, methanol, 1-propanol and 2-propanol of which the four latter liquids are used as fuels in liquid feed fuel cells. The experimental results showed that the novel meander-shaped sensor probe, for the chosen geometrical parameters, is about 17 times as sensitive to external refractive index changes than a U-bend sensor. It enabled to determination of small concentration changes in the surrounding fluid that could not be detected with common fibre optic evanescent field sensors. It was also shown that an increase in absorption length of a simple
U-bend sensor by extending the bend to a coil had only very little influence on the sensitivity, in contrast to the proposed meander shape.

Furthermore, the influence of the numerical aperture and diameter of the fibre on the sensitivity was investigated at constant bend radii, i.e., the minimum radius that could be manufactured manually. It was shown theoretically and experimentally that the sensitivity of the meander-shape sensor probe depends on all three parameters and does not necessarily increase when only one parameter is being optimised alone. Regarding the bend radius for instance, the sensitivity was shown to increase as the bend radius decreases but only down to the point where coupling between both arms of a bend occurs.

The dynamic range of bent evanescent field sensors, i.e., the measurable refractive index range, was shown to decrease with a decreasing bend radius and an increasing numerical aperture.

The sensor response was shown to be instant as refractive index changes in the surrounding medium immediately affect the penetration depth of the evanescent field into the medium and thus the loss of the optical signal guided by the fibre. The faster the sampling and data processing circuit the sooner those changes are visible in the application software. Thus, the sensor response time rather depends on the interrogation system.

The described hardware configuration used to operate the sensor is simple and easy to use. Its LED based design, in combination with an ultra-low power microcontroller unit, enables battery-powered sensor interrogation. The flexible, software-controlled, signal conditioning circuit allows to subtract signal offsets as well as to adjust the amplification factor at runtime to maximise the dynamic range of the receiver circuit, i.e., to match the intensity range of the incident light with the operating range of the analog to digital converter unit.

As of the fiber-cavity, a multimode fiber of 400µm in diameter with gold-coated end faces was used for the proof of principle. Its design enables a variety of optical fibre sensors to be operated in ringdown mode at minimum insertion loss.

The coatings on each of the fiber end faces were proven to reflect optical pulses multiple times showing the typical exponential intensity decay of ringdown cavities. The insertion loss of common fiber-cavities, almost 100%, was reduced to normal fiber coupling loss by milling a micro-hole into one of the coatings through which the light was launched into the cavity and detected at the same time using an optical time domain reflectometer. This reduction of the insertion loss is a significant improvement compared to commonly employed techniques to manufacture fibre-cavities as the need for high-power or amplified optical laser sources becomes redundant. Instead,
standard laser diodes can be used to generate the pulses and compact photodiode detectors can be used to acquire the intensity decay.

Since gold layers are highly reflective over a wide range of the infrared spectrum this type of fibre-cavity is applicable to a very wide range of applications, i.e., only the laser source and the receiver need to be selected with regard to the desired operating wavelength. For applications in the visible and ultra-violet wavelength range, other reflective materials or alloys can be coated onto the fibre ends and milled accordingly.

### 6.2 Future work

With regard to an in depth characterisation and optimisation of the proposed sensor solution, a couple of recommendations regarding future steps are given in the following section, focusing on manufacturing issues, sensor parameters and their interrogation.

#### Evanescent field sensor probe

To ensure that the geometrical parameters of every bend are identical, a proper manufacturing setup should be developed. It should also allow to bend fibres at radii smaller than 1mm in order to further increase the sensitivity of the respective probes. Once a decent manufacturing setup is in place, additional bends are the most promising way to significantly further increase the already high sensitivity but their manual fabrication has proven difficult.

The testing facilities may also be improved by means of the fluid mixing process to minimise peaks in the sensor response upon manual step concentration changes where a perfect mixing of the fluids could not be guaranteed which resulted in slight different step heights at times. A digitally controlled mixing setup would therefore facilitate automated test cycles at higher accuracy.

Future works should also include the quantification of cross sensitivities, e.g., to temperature and air bubbles. It is further recommended to investigate the upper alcohol concentration range $> 80\%$ which offers the possibility to monitor ethanol based bio-fuels. A thorough investigation of the long term stability of the LED circuit is essential with regard to a marketable product. In the same context, a pulsed signal operation is recommended to improve battery life.

#### Ringdown fibre-cavity

In terms of inserting a sensor probe into the cavity several options are feasible. Fibre-based evanescent sensors as reviewed and proposed in this investigation can be used
as well very short gaps with the absorbing flowing through. The increase in sensitivity of such sensors is directly proportional to the number of round trips of the optical pulse.

An important factor for a flawless operation of the cavity is the protection of the reflective coatings, e.g. by an additional anti-scratch coating. That will assure maximum reflection even after multiple disconnections of the fibre.

The influence of the fibre diameter on the number of round trips should be experimentally determined as different types of sensors require different fibres sizes. Evanescent field sensor probes as evaluated in this investigation show a higher sensitivity as the fibre core radius decreases while the absorption cross section of a micro gap gas or fluid cells increases with the fibre core diameter.

An alternative approach to dedicated sensor probes would be to make the coatings being the sensing elements themselves. That way the cavity loss will be minimal as no sensor element is included resulting in an increased number of reflections. A potential application in this context the monitoring of gases using a palladium alloy coating which is reflective in the near infrared wavelength region and, at the same time, sensitive to the hydrogen concentration of the ambient air. This allows for tiny tip sensors applicable in harsh environments. Hence, different coating materials offer additional areas of application, further enhancing the flexibility of the proposed cavity design.

Despite the fact that the demand for high power sources and ultra-sensitive receiver circuits, as needed with common cavities, was made redundant in this investigation, one of the remaining drawbacks of ringdown sensors is their expensive interrogation system by means of a high-speed sampling and data processing circuit for real-time operation which commonly requires bulky and expensive devices. In that context a custom DSP-operated hardware design that includes a single-shot laser driver as well as a 333MHz sampling circuit on a single PCB was described in the transfer report that summarised the interim stages of this investigation [295]. However, due to time constraints that setup could not be fully interrogated with the fibre cavity and thus was not described in the experimental setup section. It nonetheless provides a potentially compact and mobile sensor solution that reduces the costs of an overall ringdown sensor setup from several thousand Euros to a few hundred which is essential on the way to a marketable product.
Bibliography


[24] D. Sparks, D. Riley, V. Cruz, et al., “Embedded mems-based concentration sensor for improved active fuel cell performance,” in “TRANSUCERS & EU-


Appendix

1 Publications

Journal publications


Conference publications

2011


2010

2009


2008


Networks (WSNs)”, 11th Mechantronics Forum, Limerick, Ireland, June 2008

2 Key publications
Multimode fibre-optic fluid concentration sensor based on a meander-shaped sensor geometry

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Abstract A fibre-optic fluid concentration sensor based on refractive index measurements is reported. Its working principle is validated for some simple aqueous primary alcohol mixtures, i.e. acetone, ethanol, methanol, 1-propanol, and 2-propanol, covering a concentration range from 0%vol to 10%vol. With a simple and low cost LED based measurement setup, a resolution of about $5 \times 10^{-5}$ refractive index units (RIU) was achieved, which approximately corresponds to 0.2% methanol, 0.075% ethanol and acetone, and 0.05% 1-propanol and 2-propanol. Moreover, the described sensing method is applicable to all fluids that show different refractive indices at different concentrations, which by far is the case for almost all fluids as the refractive index of a mixture is related to its density.

Keywords: Refractive index sensor, optical fibre sensor, methanol, ethanol, acetone, n-propanol, water

1. Introduction

The results described in this report are based on previous works by the authors [1, 2] where a meander-shaped fibre-optic sensor probe was introduced and evaluated for different fibre core radii. A short summary is given later in this section. The present paper describes the response
of a 400 µm meander sensor tested on five primary alcohols diluted in water, i.e., acetone, ethanol, methanol, 1-propanol, and 2-propanol.

In addition to the large number of applications in the chemical industry (e.g. as solvents), these alcohols (without acetone) are also used as fuels in direct liquid feed fuel cells (DLFCs) [3], where a continuous monitoring of their concentration is essential for an optimal operation of those cells.

As a consequence of the high demand of appropriate fluid concentration sensors a wide range of approaches was reported, exploiting several physical properties of liquid mixtures. Exemplary for the case of methanol, common sensor solutions are based on the measurement of a mixture’s density [4], permittivity (relative dielectric constant) [5], viscosity [6], heat capacity [7], ultrasonic velocity (speed of sound) [8], absorptivity [9], and refractive index [10]. Furthermore, electrochemical sensors [11] as well as sensor-less prediction algorithms [12] were reported to be promising approaches for the quantification of the methanol content in the liquid feed of direct methanol fuel cells (DMFCs). Major advantages and drawbacks of the mentioned physical sensing methods are compared in table 1, mainly gathered from a review of fluid concentration sensors [13].

Table 1. Properties of physical fluid (methanol) concentration sensor approaches according to Zhao et al. [13]. (−− very poor, − poor, 0 moderate, + good, ++ very good)

<table>
<thead>
<tr>
<th></th>
<th>Sensitivity</th>
<th>Cross sensitivity</th>
<th>Response time</th>
<th>Time effects</th>
<th>Miniaturisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical</td>
<td>+</td>
<td>−</td>
<td>−−</td>
<td>−−</td>
<td>++</td>
</tr>
<tr>
<td>Density</td>
<td>−</td>
<td>−</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Capacity</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0</td>
<td>+</td>
<td>0</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>Refractive index</td>
<td>−</td>
<td>0</td>
<td>++</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>0</td>
<td>+</td>
<td>−−</td>
<td>0</td>
<td>−</td>
</tr>
<tr>
<td>Speed of sound</td>
<td>+</td>
<td>0</td>
<td>++</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>Infrared absorption</td>
<td>++</td>
<td>−</td>
<td>++</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>Sensor-less estimation</td>
<td>0</td>
<td>0</td>
<td>++</td>
<td>−−</td>
<td>++</td>
</tr>
</tbody>
</table>

Due to their lack of sensitivity, refractive index monitoring techniques are rarely applied and thus their main advantages such as the independence of electromagnetic interferences and the absence of electrical contacts remain unused. The sensor probe proposed in this report over-
Meander-shaped fibre-optic fluid concentration sensor comes the drawback of low sensitivity accompanied by an instant sensor response and tiny sensor probe dimensions.

The applied sensing method is based on the so-called attenuated total reflection (ATR) spectroscopy where the cladding of an optical waveguide is removed from a small section of the fibre so that the exposed core is surrounded by an absorbing medium (in this case a fluid). Light is launched into one end of the fibre and detected at the other end. Ideally, the detected optical power depends on the refractive index difference of the fibre core and the surrounding substance. The interaction of the light, that is confined within the optical fibre core, with the surrounding medium is achieved by taking advantage of an effect called Goos-Haenchen shift. This shift describes a phenomenon that occurs at the core-cladding interface of an optical waveguide. If a ray of light strikes this interface then the point of reflection does not equal the point of incidence but the light penetrates a few nanometers into the cladding causing an electromagnetic field called evanescent-wave field, which strongly decays exponentially with distance from the interface (evanescent literally means quickly fading away). However, by removing the cladding of an optical waveguide, the penetration depth of the evanescent field into the absorbing medium mainly depends on the medium’s refractive index and the angle of the incident ray of light at the core-medium interface [14]. Consequently, a change in the refractive index of the surrounding substance can be acquired by measuring the light intensity level at the end of the fibre. The evanescent-wave field principle is shown in fig. 1. It was shown that the sensitivity of a straight and uniform fibre probe is quite low as the angles of incident light rays with the normal to the core/cladding interface are large and thus do not approach the optimum angle of the sensing region [15], called the critical angle.

Fig. 1. Goos-Haenchen shift between an incident and a reflected ray of light at the core-cladding interface of an optical waveguide, resulting in the stimulation of an evanescent-wave field.
A common technique to increase the sensitivity is the usage of deformed fibre cores such as D-fibres [16, 17], tapers [18–20], and U-bends [14, 21, 22] because the angle at which a ray of light strikes the core/cladding interface decreases in those deformed areas, resulting in an increased penetration depth and thus in an increased interaction with the surrounding medium (higher attenuation). A more detailed description of evanescent-wave field losses on straight and bent waveguides is given in [23], supplemented by the derivation of appropriate power attenuation coefficients.

Beside using manipulated fibre core geometries, there are numerous approaches to increase the sensitivity by coating the exposed fibre core with materials that change their optical properties dependent on the concentration of the substance of interest. However, since the present paper focuses on a sensor with a wide range of fluids to be monitored, those methods will not be referred to in greater detail.

In [1] the authors compared different sensor geometries, a U-shape, a coil-shape, and a meander-shape, using 600um quartz/quartz fibres (NA= 0.22). Out of the three geometries, the latter showed a significantly greater sensitivity to aqueous methanol and ethanol solutions than the two other probes. Fig. 2 shows the gathered results for the ethanol/water case where the ethanol concentration was changed from 0% to 10%wt in steps of 1%wt. It is difficult to derive an absolute number from the figure that describes the increase in sensitivity as the concentration steps can hardly be resolved in the case of the two less sensitive probes. However, an approximate value of 16 can be determined. The hardware setup used in these previous investigations was the same as the one described in section 2.2.

Further experimental investigations regarding the influence of the fibre core diameter on the sensitivity at constant bend radii were performed in [2]. Fig. 3 shows the corresponding sensor responses of core diameters of 200um, 400um, and 600um plast clad silica fibres (NA= 0.4), at a bend radius of 1.1mm. The 400um-probe shows maximum sensitivity for the given parameters. It is expected to be exceeded by the 200um-probe for smaller bend radii, as indicated by Khijwania and Gupta in [24], but due to fabrication issues described in in section 2.1 the radius was not decreased any further. However, comparing the meander sensor response of the 600um probe in fig. 3 with the one in fig. 2, one can observe an almost 2-fold increase which is due to the as well almost two times greater numerical aperture of the fibre chosen in the second case.
Fig. 2. Comparison of the sensitivity of three different fibre core geometries using aqueous ethanol solutions covering a concentration range from 0% to 10%wt [1]. The fibre parameters are: Quartz/quartz, 600um core diameter, NA0.22.

Fig. 3. Investigation of the influence of the fibre core diameter on the sensitivity of a meander-shaped sensor probe using aqueous ethanol solutions covering an ethanol concentration range from 0% to 10%wt [2]. The fibre parameters are: PCS, NA0.4.
The refractive indices of the mixtures, which are under the scope in this investigation, versus the solute concentration (0% to 10%wt) are shown in fig. 4. For the depicted concentration range an almost linear slope in all graphs is evident which facilitates the evaluation of the sensor data later on. For higher concentrations all curves become more or less non-linear but the major number of applications is related to the lower concentration range, such as the determination of the alcohol content of low concentrated spirituous beverages or beer during fermentation or the fuel monitoring of DLFCs for instance.

![Fig. 4. Absolute refractive indices of the investigated aqueous mixtures for a concentration range from 0% to 10%wt [25, 26].](image)

Fig. 4 also reveals average refractive index changes for each integer concentration step of about $2.3 \times 10^{-4}$RIU in case of methanol, $6.4 \times 10^{-4}$RIU for ethanol, $7.1 \times 10^{-4}$RIU for acetone, $9.3 \times 10^{-4}$RIU for 1-propanol, and $9.0 \times 10^{-4}$RIU for 2-propanol. Especially in the case of methanol, the difference is very weak and requires a highly sensitive sensor to achieve proper resolutions.

2. Experiment

2.1 Sensor fabrication

Based on the above results, the sensor probe for the current investigation was fabricated using PCS fibre with a core diameter of 400 µm and a numerical aperture (NA) of 0.4.
To form the meander shape, a sufficiently long part of the fibre coating and cladding was removed from around the central position of the fibre. The exposed fibre core was then burned off in an open flame to ensure a complete removal of the cladding for an optimal interaction with the surrounding medium in later use. The uncovered fibre core was then heated with a propane flame and bent slowly until it became u-shaped. After cooling down the adjacent bends were formed. During the bending processes care was taken to maintain a constant flame temperature and bending force to ensure that the fibre core diameter itself was not compromised throughout the bent region.

The limitation of the bending radius is mainly governed by the flame dimension because if the heat conus around the flame is too wide an already existing bend will be heated and deformed again which is difficult to fix afterwards in a group of closely adjacent bends. This problem especially arises the smaller the fibre core radius is because thinner fibres require less heat to be deformed than thicker ones. Due to these fabrication difficulties and in order to be comparable with previous measurements, the bend radius was kept constant at about 1.1mm. An image of the 400μm sensing probe used for the current investigations is shown in fig. 5.

2.2 Measurement setup

In order to determine the sensitivity of the probe for the mentioned fluids, two different measurement setups were used. Broadband measurements were performed to find out sensitive wavelength(s) in the visible spectral range before narrow-band measurements were carried out at a chosen wavelength. Fig. 6 illustrates a very basic functional block diagram of the two setups.
Fig. 6. Sketch of the two measurement setups used to investigate the aqueous solutions. At first, broadband measurements were performed to discover the most sensitive wavelength (area) before narrow-band measurements were carried out at that wavelength.

Fig. 7. Block diagram of the receiver circuit used for the narrow band measurements.

The broadband measurements were simply performed by supplying the sensor probe with white light from a broadband source (deuterium-halogen lamp, DH-2000-FHSA-DUV, Micropack). On the other side a spectrometer (Ocean Optics, SR2000-TR) was used to examine the spectral behaviour of the probe under the influence of the aqueous alcohol mixtures. This was of particular interest because so called plastic fibres (POFs polymer optical fibres) were used to guide the light to the sensor and back to the spectrometer. POFs were chosen because of their low cost, compared to silica based fibres, and a sufficient low attenuation in the visible spectra range. Additionally, they show a higher flexibility and lower weight than their silicon counterparts.

The setup for the narrow-band measurements included a simple receiver circuit, mainly consisting of a UV-enhanced silicon photodiode (UVS-025), an I-to-V stage (OPA381), a digitally controlled voltage amplification circuit (PGA205), an offset reduction stage which is integrated in the PGA and a microcontroller (MSP430F169) based analog to digital conversion (ADC). The block diagram in fig. 7 shows the described setup.

The dimensioning of the receiver circuit’s I-to-V stage is shown in the respective graphs of the results section. For referencing purposed two
identical receiver circuits were incorporated in the hardware setup but the reference channel was not used in this investigation. The setup is simple to operate and reconfigurable due to the microcontroller based hardware environment and enables low cost continuous fluid concentration monitoring.

3. Results

In analogy to the previous reports, a concentration range from 0% to 10%vol was used to evaluate the sensitivity of the sensor probe for the different liquid solutions, increased in steps of 1%vol in each case. The results of the broadband measurements are shown in fig. 8 to 12, carried out at an ambient temperature of 20°C.

Fig. 8. Measured spectra of 1-propanol/water at 20°C.

The spectra at 0% solute concentration were taken as reference spectra and divided by the following spectra of increasing concentrations. Since the refractive indices of the mixtures increase with the solute concentration (fig. 4), the light intensity that is acquired at the end of the fibre decreases at the same time, causing the relative intensities shown in the spectral graphs to increase.

As expected from the refractive index graphs in fig. 4, 1-propanol shows the highest attenuation of all mixtures and methanol the lowest. Therefore, the sensor resolution with regard to fluid concentrations is different for each mixture. Similar for each of the investigated solutions
Fig. 9. Measured spectra of 2-propanol/water at 20°C.

Fig. 10. Measured spectra of acetone/water at 20°C.
Fig. 11. Measured spectra of ethanol/water at 20°C.

Fig. 12. Measured spectra of methanol/water at 20°C.
is the shape of their relative spectra but that is mainly due to the attenuation properties of the fibres that were used.

However, a decreasing sensitivity is evident for wavelengths below 475nm, which is due to an increasing attenuation of both the PMMA-POFs (polymethylmetacrylate) and the PCS fibre. The graphs further reveal a local sensitivity minimum at about 625nm, explained by a peak in the attenuation spectrum of the PMMA-POFs. Above 675nm there is a strong decrease of the relative intensity again caused by an attenuation peak of the PCS fibre (not shown in the graphs). However, a wide range of the visible (VIS) spectrum can be used to monitor the investigated fluids and there are low cost LED light sources available in this wavelength range as are appropriate photodiode detectors.

For comparison reasons with previous results, a wavelength of 650nm was chosen for the narrow-band measurements, yielding a higher intensity resolution compared to the spectrometer. In accordance to fig. 2 and 3, the solute concentrations were changed in steps of 1%vol (upper x-axis) every two minutes (lower x-axis). The resulting graphs are shown in fig. 13.

![Fig. 13. Sensor response to step concentration changes (1%vol) of acetone, ethanol, methanol, 1-propanol and 2-propanol in water at 650nm/20°C. The graph shows the change in the output voltage of the I-to-V stage which was dimensioned as indicated in the figure.](image-url)
The y-axis shows the change in the output voltage of the I-to-V stage without further amplification. The graphs are in almost perfect accordance to the refractive index curves in fig. 4 by means of the slopes and the ratios between the slopes of each curve.

Based on the result shown in fig. 13, the resolution of the sensor was found to be approximately $5 \times 10^{-4}$ refractive index units which approximately corresponds to a methanol concentration of 0.2% vol, an ethanol and acetone concentration of 0.075% vol and a 1-propanol and 2-propanol concentration of about 0.05% vol.

However, the refractive index of a liquid solution is not only a function of its compound concentrations but of temperature as well, described by the temperature coefficient $dn/dT$ which quantifies the change in the refractive index per unit temperature (usually $1^\circ C$). Table 2 summarizes frequently cited literature values of $dn/dT$ of the fluids used in this investigation.

Table 2. Temperature coefficients of the refractive indices $dn/dT$ of the fluids under scope in this investigation.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$-dn(10^{-4})/dT(^\circ C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>4.9 [27], 5.0 [28]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.6 [27], 3.9 [29, 28, 30], 4.38 [31, 30], 4.53 [30, 32]</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.9 [29, 27, 28, 30, 33], 4.32 [30, 32]</td>
</tr>
<tr>
<td>1-propanol</td>
<td>3.8 [27], 3.9 [29, 30, 32], 4.33 [30, 32]</td>
</tr>
<tr>
<td>2-propanol</td>
<td>3.4 [34], 4.63 [32]</td>
</tr>
<tr>
<td>Water</td>
<td>0.8 [29, 30], 0.99 [35], 1.04 [27, 30]</td>
</tr>
</tbody>
</table>

The drifts mainly referred to are: $-5.0 \times 10^{-4}/^\circ C$ (acetone), $-3.9 \times 10^{-4}/^\circ C$ (ethanol, methanol, propanol), and $-1.0 \times 10^{-4}/^\circ C$ (water). With these values known, temperature drifts can be compensated for but since these values refer to the pure components, they must be weighted according to the compound concentrations:

$$\frac{dn}{dT} = x_1 \frac{dn_1}{dT} + x_2 \frac{dn_2}{dT}$$

(1)

where $x_i$ is the weight fraction of compound i and $dn_i/dT$ the temperature coefficient of the index of refraction of the pure component i of the mixture.

Another way of correcting temperature drifts is the acquisition of a comprehensive set of solution refractive indices at different temperatures and compound concentrations. Openhaim and Grushka [36], for
instance, published an appropriate data set for aqueous methanol mixtures. However, such measurements are quite extensive and result in a fitting equation of two dependent variables.

4. Conclusion

It was shown that continuous fluid concentration monitoring at high sensitivity is possible with a simple and low cost optical fibre sensor application. The working principle was verified by evaluating the sensor response for different liquid solutions with, to some extend, very low refractive index changes per integer concentration step as in the case of methanol/water. The application range of the presented sensor probe is not limited to the investigated mixtures only but to all fluids that show a change in refractive index as the compound concentrations vary.

References


Meander-shaped fibre-optic fluid concentration sensor


Optical fibre cavity for ring-down experiments with low coupling losses

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Abstract
A fibre-cavity design based on highly reflective gold coatings, vapour deposited to the two end faces of a large core multimode waveguide, is presented. In contrast to common fibre-cavity approaches, the laser pulses are not coupled through the reflective coatings into the cavity but through a micro hole in one of the fibre end faces, which reduces the commonly very high coupling loss to less than 1%. Accordingly, lower demands on the source power and the sensitivity of the receiver circuit result in lower costs of ring-down sensor approaches. The scope of the paper is on the proof of principle and the characterization of the novel fibre-cavity design. Nevertheless, potential applications are briefly addressed at the end of the paper.

Keywords: ring-down spectroscopy, fibre cavity, optical fibre sensor

(Some figures in this article are in colour only in the electronic version)

1. Introduction
A crucial part of applying ring-down sensing techniques to optical fibres is the design of appropriate fibre cavities. Early investigations by Stone and Marcuse comprised highly reflective external mirrors, which were placed adjacent to the polished fibre ends but this method turned out to be susceptible to external vibrations [1]. Later on, metallic coatings were directly vapour deposited to the fibre end faces, resulting in reduced mirror coupling losses and a lower sensitivity to mechanical vibrations [2]. In a similar approach, these metallic coatings were replaced by multilayer dielectric coatings and applied to evanescent-field sensing [3, 4], for instance. To overcome the drawback of surface roughness due to imperfect polishing of the fibre ends, fibre Bragg gratings were used as reflective elements [5–7]. Another widely investigated approach, using fibre loops (fibre-ring cavities) instead of reflective layers, is the subject of many publications to date and was proven to be suitable for many sensing purposes such as fluid monitoring [8, 9], trace gas detection [10], temperature [11], pressure [12], force [13], and strain sensing [14], as well as refractive index measurements [15].

A major drawback that all the above approaches have in common is an almost 100% coupling loss when light is coupled into the cavity, either through the reflective layers ($R > 99.9\%$) or by using couplers of high split ratios (e.g. 99:1) in the case of fibre loops. Since the photodetector is commonly located behind the second mirror of the same reflectivity or another coupler, a maximum of about 1/10 000 of the initial pulse intensity can be detected in the case of passive non-resonant cavities. In the case of time resolved ring-down signals, this initially received intensity is even less with each round trip. On the other hand, the high reflectivity or coupling ratios are necessary to achieve large numbers of round trips, a high cavity finesse. Thus, pulses of high intensity and highly sensitive photodetectors or optical amplifiers within the cavity are used [10, 15]. Although ring-down methods have shown great potential for high sensitivity detection, their use to date has been confined largely to the research laboratories. For this reason, our major concern was to design a fibre cavity that reduces the hardware requirements with respect to pulse intensity and receiver sensitivity to make all the potential applications above widely applicable.
2. Results

The significant decrease of the coupling loss of the incident laser pulse was achieved using a multi-mode fibre whose end faces were sputter coated with a 120 nm gold film. A micro hole of 10 μm in diameter was milled into the coating at the centre of one of the fibre end faces (figure 1) using focused ion beam technology (FEI FIB 200, 50 nm beam diameter, 50% overlap, 1 ms dwell time, 3 min milling time). A single-mode fibre (Corning SMF-28) was attached to the multi-mode cavity using SMA connectors. The parameters of the 20 m long 3M™Polymer Clad Silica (PCS) fibre the cavity consists of are as follows: core diameter = 400 μm, NA = 0.4, core refractive index = 1.457, cladding refractive index = 1.401, step index profile.

Once a transversal single mode was coupled into the multimode fibre through the micro hole, many modes were excited which is the basic principle upon which the proposed fibre cavity is based. Figure 2 shows this principle using the model of light as rays propagating on a zig–zag path along the fibre core. In figure 3, the excitation of higher order modes is shown by means of the electric field distribution versus the fibre-core radius at different distances from the coupling point using a two-dimensional simulation approach. It can be seen that with increasing distance the intensity decreases in the centre region of the core but the pulse broadens in the spatial dimension until it spreads the entire fibre core after just a few millimetres. If the spatially broadened pulse now strikes the coating that includes the micro hole, then it is clear that just a small portion of the overall intensity leaks out the cavity, whilst the much greater portion is reflected by the coating that surrounds the micro hole. After a pulse is reflected and the intensity in the centre of the core is lost, energy exchange between adjacent modes then results in a ‘uniform’ field distribution again after a few millimetres but with a decreasing amplitude. The decaying pulses can be acquired through the same hole that was used to couple the light into the fibre, as indicated in figure 2, or through another hole on the other side of the fibre, which implicates slightly increasing losses per round trip.

The initial proof of principle measurements was performed using an OTDR (optical time domain reflectometer, EXFO IQ-7000, 10 ns pulse length) at 850 nm. The fibre attenuation at 850 nm is about 17 dB km⁻¹. As the pulse length is short with respect to the cavity length, it is assured that there are no disturbing superposition effects caused by temporal pulse broadening due to dispersion. A single mode ‘dummy’ fibre (Corning SMF-28) of 1 km in length was placed between the OTDR and the fibre cavity to avoid OTDR ghosts in the OTDR trace for 2 km as they could interfere with the decaying pulses. The resulting OTDR trace is shown in figure 4 (including all significant parameters), starting with the first received pulse that was reflected by the cavity. The expected decay of pulse peaks is observable with a loss per round trip of about 1 dBm (0.68 dBm due to the fibre attenuation and 0.32 bBm due to reflection and micro hole losses) but the
pulses do not reach the noise level as can be seen in the full OTDR trace in figure 5. We believe that this effect is due to the influence of the dummy fibre whose entire trace appears as a kind of an offset after 1 km. Consequently, the shape of the decay function could be disturbed and additional pulses of lower intensity may be overlaid by the offset and thus do not appear in the graph. Further, limiting effects with respect to the number of reflections are the low input power (−20 dBm) caused by a 50 μm/10 μm interface at the OTDR output as well as the relatively high detection limit of the OTDR receiver (−35 dBm) which is far above that of common photodiode receivers. Thus, the dynamic range covered in the experiment is about 15 dB only. For this reason, further investigations using an improved source and receiver circuit are required. However, these preliminary results are very promising to reach similar results to those of other fibre cavities but with less source power and low-cost photodetectors, hence, a much cheaper experimental setup. However, going back to the OTDR trace in figure 5, there is a fast decaying ring-down curve. Consequently, n in equation (2) can be replaced by \( \frac{c}{2n_{\text{co}}L} \), resulting in equation (3) which now is dependent on time:

\[
I(t) = I_s \exp \left( -\frac{t}{\tau} \right) \\
\simeq I_s \exp \left( -\frac{c}{2n_{\text{co}}L} \left( -\ln(R_1R_2) + 2\alpha L \right) \right). 
\]

Assuming such a single exponential decay function, it is clear from equation (3) that the decay time constant \( \tau_0 \) of the fibre cavity without any sensor probe yields

\[
\tau_0 = \frac{2n_{\text{co}}L}{c_0 \left(-\ln(R_1R_2) + 2\alpha L \right)}. 
\]

If a sensor element of length \( L_1 \) is inserted into the cavity, an additional loss of \( \alpha_1 \) will be induced into the cavity (equation (5)) resulting in a faster decaying ring-down curve. Dependent on the sensor element, the term \( \alpha_1 L_1 \) can be expressed in many different ways. However, the focus of the present paper is on the characterization of the novel cavity design. Thus, the influence of potentially applicable sensor elements on the overall loss is kept in the general term above:

\[
\tau = \frac{2n_{\text{co}}L}{c_0 \left(-\ln(R_1R_2) + 2\alpha L + 2\alpha_1 L_1 \right)}. 
\]

It is common to refer the expression \( \ln(R) \) to \( -(1 - R) \) for a reflectivity close to 1, where \( R = R_1R_2 \) in the present study. Finally, the influence of the micro hole on the reflectivity of the entire fibre end face has to be taken into account. Assuming a uniform intensity distribution over the entire fibre-core radius, a simple additional factor can be multiplied with the reflectivity of the coating \( R_1 \) to yield an expression for the overall reflectivity. This additional factor represents the
In order to choose the best coating material for the desired operating wavelength, the wavelength dependence of the reflectivity of several metals is shown in figure 7, with sufficient large values above the visible spectral range in the case of gold and silver. Noble metals are favourable as they are non-corrosive. For applications in the visible spectral range, there are many alloys of higher reflectivity than those of pure metals.

Since the reflectivity of gold (and the other metals) is a function of the layer thickness as well, a sufficient thick film has to be coated onto the fibre ends. According to Miller and co-workers, the maximum reflectivity of gold layers is reached at about 25 nm thickness in the near-infrared region [16]. Other (unreferenced) sources show values about 80 nm but without a corresponding wavelength. However, the layer thickness of the present study has been chosen to be about 100–120 nm to ensure maximum reflection.

In terms of potential applications of multi-mode cavities in optical-fibre sensing, several proven approaches shall be referenced. A quite recent sensor design deals with micro-fluidic and micro-optic gas cells. Andachi et al used a micro-fluidic cell with a 100 μm gap (50 μm core) to monitor the content of methylene blue dye in water [7]. Capillary electrophoresis absorption detection was a fibre ring [18]. A very short gap of only 3.8 μm (50 μm core) was used by Brown et al for organic dye absorption spectroscopy [19]. Atherton and co-workers frequently applied micro-optic gas cells inserted into a fibre loop (50 μm core) [20]. The above examples would benefit from the proposed cavity as it provides a larger fibre core which facilitates fibre alignment and could span greater distances (still in the micrometer region of course). Another type of sensor which has been proven to be suitable for use in combination with fibre cavities is the so-called taper, extending the range of applications to evanescent field absorption sensing [9], strain sensing [21] and biosensing [22]. Finally, two especially designed sensor heads for particular purposes shall be mentioned which were combined with multi-mode fibre cavities, e.g., a direct current (dc) sensor [23] as well as a pressure sensor [24]. The latter publication is of special interest since it compares the results of a single-mode setup with a multi-mode design, finding the multi-mode sensor to be more sensitive.

3. Conclusion

It was shown that the coupling loss of fibre cavities can be significantly reduced from almost 100% to less than 1% by using the proposed multimode cavity design. A major advantage of the decreased loss is the ability to use standard low-power laser diodes resulting in cost reduction, potential miniaturization and improved robustness of the system. Common photodiodes with low feedback resistors can be applied which increases the system stability compared to large resistor values. Finally, multimode sensors generally achieve higher sensitivities than their single mode counterparts due to the presence of more modes that interact with the substance under study.

References


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