Distributed plastic optical fibre measurement of pH using a photon counting OTDR

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Abstract. Distributed measurement of pH was demonstrated at a sensitised region 4m from the distal end of a 20m length of plastic optical fibre. The cladding was removed from the fibre over 150mm and the bare core was exposed to an aqueous solution of methyl red at three values of pH, between 2.89 and 9.70. The optical fibre was interrogated at 648nm using a Luciol photon counting optical time domain reflectometer, and demonstrated that the sensing region was attenuated as a function of pH. The attenuation varied from 16.3 dB at pH 2.89 to 8.6 dB at pH 9.70; this range equated to –1.13 ± 0.04 dB/pH. It is thus possible to determine both the position to ±12mm and pH to an estimated ±0.5pH at the sensing region.

1. Introduction
Optical Time Domain Reflectometry (OTDR) is well known as a method of detecting breaks in long lengths of telecommunications fibres [1, 2]. A light pulse is launched into an optical fibre; and undergoes scattering along the fibre length due to impurities or microscopic density fluctuations. A proportion of the light is backscattered towards the input causing a reflected pulse to be detected at the input with total time duration of that taken for light to travel through twice the total fibre length. OTDR has been used to measure attenuation in distributed optical fibre sensors based on silica or polymer clad silica (PCS) fibre [3]. To date, no optical fibre sensor has been demonstrated using OTDR on plastic optical fibre (POF). Luciol Instruments have developed a photon counting OTDR (υ-OTDR) specifically for POF to analyse short-range data transmission networks using visible light [4].

POF has a typical attenuation of 200dB/km at 650nm compared to silica fibre that has an attenuation of less than 0.2dB/km at 1550nm. However, new manufacturing processes and materials have enabled graded index POF with attenuation of 79dB/km at 650 nm and gigabit transmission over 300m [5] encouraging POF possibilities for distributed sensing. POF is inexpensive, rugged and does not suffer the problematic cleaving and poor coupling that is associated with glass fibre. The low fabrication temperatures of POF enable organic chromophores and rare earth organic metallics, that would be destroyed by the high temperatures used in glass fibre production, to be added to POF facilitating incorporation of fluorophores and chemical indicators. Most importantly, previous work by the researchers has demonstrated that evanescent POF sensors based on multimode large diameter fibre, are an order of magnitude more sensitive than multimode evanescent glass fibre sensors and can sense parameters such as refractive index, strain, turbidity, scaling, biofouling, flow and strain [6-10]. For evanescent field sensors, the proportion of light, available to interact with the measurand in the evanescent field is less than 1% for weakly guiding multimode fibres such as 200µm diameter PCS fibre. The evanescent field power can be maximised by exciting high order modes to optimise the
penetration depth and increase the sensitivity of the sensor, but POF is widely available in large diameters, typically 1 mm and thus will support tunnelling rays in addition to bound rays [7, 9, 10]. The researchers have demonstrated that for POF evanescent field sensors, tunnelling rays contribute an extra 50% to the energy available for modulation by the measurand in the evanescent field. At the distal end of the fibre, it is shown that 66% of power is contained in the bound modes and 33% in tunnelling modes; enabling maximum modulation of the signal of typically up to 13%, indicating that 13% of the total guided power exists in the evanescent field [7, 9]. Thus it seems clear that despite high attenuation, an order of magnitude of three times worse than silica fibre, POF redeems itself with an order of magnitude greater sensitivity to evanescent field modulation. Consequently, the aim of this work was to demonstrate a POF sensor using OTDR.

2. Photon Counting OTDR

The OTDR used was a commercially developed instrument by Luciol for POF applications using a 648nm laser light source and a photon counter detector based on an avalanche photodiode. Most proprietary OTDR instruments employ analogue detection of backscattered light signals, however Luciol’s u-OTDR treats the signal as a string of photons separated by variable time intervals [4], each photon detected giving a pulse equivalent to a binary “1”. The laser diode emitted pulses of 1.5ns duration and 3nm full width half maximum. The instrument was specified to have a spatial resolution of less than 5mm for one point, less than 10cm for two-point spatial resolution (discrimination) and 25dB dynamic range for wavelengths below 900nm. However, the customised u-OTDR configuration used for the work described in this paper was designed to return a higher Rayleigh backscattered signal at the expense of poorer resolution values. Therefore, the first step in the investigation was to measure the one- and two-point spatial resolution values. The dynamic range of 25dB determines the maximum length of the fibre that can be interrogated. At 650nm, poly methyl methacrylate (PMMA) core POF has an attenuation of around 200dB/km; 100m of undoped Mitsubishi CK40, for example, would use up most of the dynamic range budget, with a margin for losses due to inline connectors. However, a distributed optical fibre sensor (DOFS) will contribute additional attenuation that can be limited to a short length over which a measurand acts, or over the whole fibre length. It was estimated that the Luciol u-OTDR could interrogate PMMA POF from 50 to 100 metres.

The Luciol OTDR has a sliding measurement window to maximise the dynamic range; it is possible to exclude Fresnel reflections from internal fibre links and the front panel connector.

3. Measurements of Spatial Resolution and Discrimination on Luciol u-OTDR

Figure 1 Luciol OTDR interrogation of CK40 POF by 650nm radiation
There are a total of six Fresnel reflections. Point A is that from the fibre end at the detector, B is from the front panel connector, C is from a male-female patch connector pair, D and E correspond to the butt joints either side of a short link fibre (41cm) and F is the end of fibre Fresnel reflection. F corresponds to a total length outside the OTDR unit of 25m. It can be seen that the fibre between points E and F is close to the noise floor; since the dynamic range budget is used up by including the Fresnel reflections at the start of the fibre, i.e. points A, B and C. The points D and E are resolved as two separate peaks but the modulation is reduced indicating that as the fibre length decreases, the trace tends to a single distorted peak. The peaks are shown in detail in Figure 2.

![Figure 2 Detail of Peaks Corresponding to Butt Joints](image)

The fibre configuration was changed so that the spacing fibre was 25m from the front panel and the total fibre under test was 62m. Figure 3 shows a section of the fibre trace with initial Fresnel peaks excluded, by programming a start delay of 15m to move the dynamic range window to the region of interest. Two spacer fibre lengths of 41cm and 78cm respectively were assessed with this new configuration. The traces of the spacer fibre placed within a total length of 62m are shown in Figure 3. The trace from the 41cm spacer fibre forms a single peak. When a 78cm spacing fibre was placed in the link, the trace forms a single peak with a shoulder instead of two peaks. In order to assess one point resolution, it must be noted that the ability to sense stimuli applied to different positions on the fibre at different times in terms of repeatability and the difference values between different positions are more important than absolute accuracy. This was assessed by using two tape markers 20cm apart according to a ruler (error ± 1mm) were applied to the fibre under test, the closest to the launch end at a nominal distance of 17.34m. A point bending force was applied to each marker in turn and the length difference computed and the operation repeated a further nine times. The mean difference was 18.80cm, standard deviation 0.42cm.
4. Theory of Evanescent Wave Absorption using a Multimode Optical Fibre

The Beer-Lambert Law relates the absorbance, $A$, of a liquid to molar absorptivity in L mole$^{-1}$ m$^{-1}$, $\varepsilon$, concentration, $C$, in mole L$^{-1}$ and path length, $L$, in metres by $A = \varepsilon CL$. This equation can be modified for the special case of declad optical fibres. Included is a coefficient for the geometry of the waveguide, $G$, $A = \varepsilon CLG$. The coefficient, $G$, is only valid for meridional rays which restricts the quantitative validity of the model. In practice the absorbance of the sensor also depends on skew rays and tunneling rays, as discussed in Section 1. The waveguide geometry coefficient has been modeled for meridional rays [9].

5. Distributed Optical Fibre Sensing of pH

The evanescent field of a fibre can be exposed to a measurand in three ways: removal of the cladding, substituting a doped responsive cladding and impregnating the cladding with a dye. Removal of the cladding should be avoided for a distributed fibre, since a declad fibre is very lossy. The original cladding of a PCS fibre was retained and impregnated with chemical specific dyes so that the silicone cladding acts as a permeable matrix [11-13]. A POF sensor with a section of cladding removed and replaced with a thin layer of methyl red doped PMMA [14]. For the work reported here, a simulated distributed sensor was constructed by choosing one position along a 25m length of untreated CK40 POF and removing the cladding by acetone over a 150mm length [15]. The sensitised site was 4 metres from the end of the fibre. The bared-core fibre was immersed in a 0.00042 M aqueous solution of methyl red and the pH was varied by addition of drops of concentrated hydrochloric acid or 0.880 S.G. ammonia and monitored independently by a Hanna Instruments pH Checker. OTDR traces were captured when the sensing site was exposed to three values of pH (Figure 4). A start delay was used to exclude the front of fibre Fresnel peaks, point A defining the end of the blanking period. Point B shows a kink in the fibre to act as a marker. Point C corresponds to the 150mm region where the cladding has been removed and point D is the end of fibre Fresnel reflection. It can be seen that as the attenuation increases with decreasing pH value at point C increases.

Methyl red is a well-known pH indicator that changes colour from yellow (alkaline) to red (acid). The 650nm red light launched into the fibre is absorbed more at low pH. The experiment was repeated with the identical test fibre immersed in distilled water, whose hydroxyl ion concentration was

![OTDR Interrogation CK40 POF with Spacer Fibres between Butt Joints](image-url)
adjusted to three similar values of pH. The change in attenuation as a function of pH was not resolvable. The absorption spectrum of the aqueous methyl red solution at identical pH values were measured by a Shimadzu UV-2401PC Spectrometer over the range 400 to 900nm, and absorbance at 650nm are recorded in Table 1.

| pH  | Absorbance at 650nm |
|-----|---------------------|
| 9.10 | 0.0245              |
| 6.35 | 0.042               |
| 3.05 | 0.9485              |

Table 1 Shimadzu UV-2401 Spectral Analysis of Aqueous Methyl Red Solution

There is a significant increase in absorbance at 650nm as the solution becomes more acid. This would explain the higher attenuation experienced by the POF in increasingly acid methyl red environments.

6. Discussion and Conclusions
The assessment of one-point spatial resolution of the Luciol u-OTDR showed that a measured difference of 12mm was close to the manufacturer’s specification of 5mm; this is sufficient for a distributed fibre of tens of metres. This compares favourably with the typical specified sampling resolution of 40 to 80mm for analogue OTDRs. A measurand applied over a declad region 150mm long can be identified due to the attenuation. The assessment of two-point spatial resolution showed that the position of the two closely spaced stimuli could be discriminated to within 40cm, but 20m away, the discrimination had degraded to 80cm or more. The manufacturer quotes a discrimination of <10cm, but resolution would be degraded by increasing the Rayleigh backscattered signal. Resolution deteriorates away from the launch point due to the high values of modal dispersion associated with POF.

A distributed POF pH sensor has been demonstrated by decladding a short length of POF and exposing the core to aqueous methyl red solution over a range of pH values. POF has a fluorinated PMMA cladding that required careful removal; the peak at point C in Figure 4 may be due to a core
surface roughened by acetone. Fluorinated PMMA is impervious to doping so future work includes investigation of optical fibre comprising a PMMA core clad with silicone resin; providing all the advantages of POF, but permitting ingress of dyes into the silicone resin matrix to exploit the evanescent wave absorption effect. There is also scope for further work in the investigation of any surface adsorption at the core-solvent interface.

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