A Novel Waveguide Configuration for Convenient and Sensitive Fluorescence and Raman Measurements of Liquids Over Optical Fibers

Steven J. Mackenzie\textsuperscript{a}, Mark Johnson\textsuperscript{b}, and John P. Dakin\textsuperscript{c}
\textsuperscript{a}The Optoelectronics Research Centre, Southampton University, UK, SO17 1BJ
\textsuperscript{b}North West Water Ltd, Dawson House, Warrington, UK, WA5 3LW
\textsuperscript{c}Department of Electronics and Computer Science, Southampton University, UK, SO17 1BJ

ABSTRACT

Fluorescence has been measured from a waveguide formed by a PTFE tube with an internal coating of a low-refractive-index amorphous fluoropolymer. The configuration is suited to taking measurements from liquids having a refractive index down to 1.32, including, in particular, aqueous solutions. The parameters which determine the optical collection efficiency have been mathematically modelled. We have produced waveguides up to 1 m long, and with 0.955 mm and 0.445 mm internal radii, and measured a (fluorescence) collection enhancement factor of 3 from a 140 mm long, 0.955 mm internal radius waveguide. Work is continuing to increase the enhancement factor.

Keywords: water, aqueous, fluorescence, Raman, optical fiber, spectroscopy, Teflon-AF

1. INTRODUCTION

Measurements of optical emission, such as Raman scattered light or fluorescence, are widely used in chemical analysis. However, measurements of low intensity emission require that maximum use is made of all the available light.

In order to increase the total amount of light collected in emission spectroscopies, optical fibre probes have been coupled to capillary-waveguide cells. If the refractive index of the capillary is lower than that of the analyte, then a waveguide is formed, and light will be tightly confined within the analyte. Scattered light will be most efficiently coupled into the probe when the capillary diameter matches the probe diameter. By using very long capillaries this arrangement can increase the signal collected by several orders of magnitude\textsuperscript{1}.

Unfortunately this approach was not possible for many liquids (including most aqueous solutions), because the refractive index of most capillary materials is too high to form a waveguide; for instance, silica glass has $n=1.47$. Poly [tetrafluoroethylene] (PTFE)\textsuperscript{2} has $n=1.34$ but strongly scatters light due to its semi-crystalline structure. We have proposed two cell designs which are compatible with the use of this waveguiding approach for the analysis of lower refractive index solutions.

In one method, to be presented later at this conference\textsuperscript{3}, the need for cladding the waveguide has been dispensed with altogether. By shaping the falling analyte into a cylinder surrounded by air, light is reflected at the boundary between the analyte and air by total internal reflection, and the analyte alone forms a very efficient waveguide. We studied stable falling analyte streams, produced using nozzles of internal diameter 1.0, 1.5, 2.0, and 2.5 mm. Light was coupled in and out of the base of the stream with a multiple optical fibre probe.

The method presented here is to use a capillary tube internally coated with a low-refractive-index polymer. The coating material, Du Pont Teflon AF-1600, is a copolymer of PTFE and poly [2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole] (PDD), with a particularly low refractive index of 1.32, which is suitable for forming low-index cladding tubes. Unfortunately it is expensive (~US$40/g), and requires specialised processing to fabricate complete cladding tubes. We have overcome these problems by simply depositing a thin film up to 15 µm thick on to the inside of a
commercial PTFE support tube.

This paper describes our efforts to fabricate such cells up to 1 m in length, and our investigations into the utility of such an arrangement for fibre-remoted spectroscopic measurements. The main difficulty encountered so far has been in achieving films of consistent thickness and surface quality, which has resulted in lower than expected waveguide transmission and fluorescent collection enhancement.

1.1. Teflon-AF amorphous fluoropolymer

The copolymers marketed by the Du Pont company under the trade name “Teflon” typically consist of more than 90% of the monomer TFE, with comonomers introduced to reduce the crystallinity and shorten the length of the poly(tetrafluoroethylene) chains within the compound. The copolymer is then more amenable to thermal processing or solvation in certain solvents. However, any crystallites formed in the copolymer are optically scattering. These polymers are renowned for their low surface energy, chemical inertness, and strength. The Teflon-AF brand shares these properties, but it is unique among the Teflon compounds because it is optically transparent, with much lower scattering, and unique among solid polymers, having a refractive index of less than 1.32.

Teflon AF is a copolymer of TFE and PDD (see figure 1), and typically comprises 60% PDD, or more. It is the ring structure of PDD which prevents crystallinity, and hence renders the copolymer optically transparent over the whole visible region, extending to approximately 2.7 µm in the near infrared. In addition, the PDD ring structure results in nano-voids in the copolymer, so that the refractive index of the resulting compound is significantly lower than other materials. Two variants of Teflon AF are readily available, AF-1600, and AF-2400, having glass transition temperatures of 160ºC and 240ºC, and refractive indices of 1.312 and 1.295 respectively.

Teflon AF copolymer can be processed by compression moulding, or may be deposited from solution in certain fluorinated solvents, the approach taken in this work. We have used AF-1600, because it was available in a more concentrated solution. In earlier work, we deposited the films from solution in FluorInert FC75 (ICI, UK), a totally fluorinated compound, onto silica glass capillary tubes. We found that, despite pre-treating the silica surface with a fluoro-silane compound (the tubes were boiled under reflux for 1 hour in a 0.5% solution of 1H,1H,2H,2H-perfluorodecytriethoxysilane in methanol), adhesion of the films was poor in the presence of water. In fact, tubes of Teflon AF with approximately 10 µm thick walls could be formed by leaving internally-coated glass tubes submerged in water for an hour or so. The water migrated between the silica and the fluoropolymer coating, and the fluoropolymer tube was released. It could eventually be gently pulled out by hand, and left to dry in air.

Layers of Teflon AF deposited onto a PTFE substrate are much more stable however, and in this paper we describe how we fabricated capillary cells, and how they perform as optical waveguides and as spectroscopic cells.

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*Since this work was started, we have noted that a similar configuration is available commercially from World Precision Instruments, FL. They supply a 50 cm long 0.39 mm diameter cell, designed to interface to their range of miniature fibre optic spectrometers.*
2. THEORY

In this section, we develop a mathematical model to describe a capillary waveguide as a spectroscopic cell, and estimate the thickness of the Teflon AF layer that is required for acceptable performance.

2.1. Collection enhancement factor

In our analysis we assume that the waveguide-capillary cell (the waveguide) is cylindrical, and the excitation and collected light enters and leaves the cell via an optical fibre probe (the probe) with a circular aperture, which is centred on the cylinder axis, as shown in figure 2. The probe aperture is assumed to be smaller than the cylinder cross section, and to accept light over a smaller, or equal, range of angles to that guided by the liquid-cored waveguide. Emission from the analyte is assumed to be isotropic, a reasonable assumption for the small range of angles, 0 to $\theta_{\text{inlet}}$, over which it is confined within the waveguide. Only light that is fully guided by the probe is considered here; it is well known that some unguided, or leaky, optical fibre modes can propagate very efficiently over short distances, so we expect to derive an underestimate of the total collected flux $^7$.

![Figure 2](image-url) A depiction of the coupling between the probe and the waveguide. (An incremental quantity of collected flux, $d\Phi$, is considered to originate from the thin slice of thickness $dz$. The refractive index of the Teflon AF1600 wall is 1.312 in the visible region, while the refractive index of water is 1.333.)

Within the waveguide, any light making an angle of less than $\theta_{\text{analyte}}$ to the axis will undergo repeated total internal reflection, where $\theta_{\text{analyte}}$ is equal to $90^\circ - \theta_c$, and $\theta_c$ is the critical angle given by Snell’s law. The numerical aperture $NA$ of any optical element is defined in equation 1, where $\omega$ is the maximum ray angle accepted by the element, and $n$ is the refractive index of the medium in which the ray is travelling. A water cored waveguide formed with Teflon-AF 1600 cladding has an $NA$ of 0.22. In this work, resolution requirements set by the spectrograph limited the useful $NA$ of the probe to 0.17.

$$NA = n \sin(\omega)$$

(1)

Excitation light diverges from the probe until it intersects the waveguide wall, at the point marked $z_i$ in figure 2. Because the waveguide $NA$ is less than that of the probe, the light is reflected back towards the centre of the waveguide. Fluorescent or Raman light is emitted within the cylinder, and some of this light will follow the reverse path back to the probe.

The proportion $S$ of the light emitted by the analyte that is guided towards one end of the waveguide is given by equation 2.

$$S = \frac{2\pi (1 - \cos(\omega_{\text{analyte}}))}{4\pi} = \sin^2\left(\frac{\omega_{\text{analyte}}}{2}\right)$$

(2)

For a waveguide having a water core, and a cladding of AF-1600, $S$ is equal to 0.0071. The most efficient means of coupling light to the spectrograph was to insert a single fibre optical probe into the liquid-cored waveguide. For a collection aperture perfectly matched in size to the water cylinder cross section, the coupling efficiency $\eta_{\text{col}}$ between
them is given by equation 3,

\[ L_{\text{NA}} = \frac{\Omega_{\text{input}}}{\Omega_{\text{analyte}}} = \frac{4\pi \sin^2(\omega_{\text{input}}/2)}{4\pi \sin^2(\omega_{\text{analyte}}/2)} \]  

(3)

where \( \omega_{\text{input}} \) is the half-cone angle of the probe, \( \Omega_{\text{input}} \) is its solid angle, and \( \Omega_{\text{analyte}} \) is the solid angle of light guided within the waveguide.

In the case where the waveguide cross section is larger than the probe aperture, the coupling efficiency due to radius mismatch is given by equation 4.

\[ L_{\text{radius}} = \frac{a^k}{R^k} \]  

(4)

Here \( a \) is the probe radius, \( R \) is the waveguide radius, and \( k \) is a constant between 1 and 2 which depends on the distribution of scattered light within the waveguide. A value of \( k=1 \) represents the case where all rays pass through the waveguide axis, whereas \( k=2 \) represents the case where skew rays carry an equal amount of energy (ie all waveguide modes are equally excited). In these experiments, the excitation light was delivered to the waveguide under the conditions for \( k=1 \), and if the Teflon-AF was perfectly smooth we could expect the emitted light to have a similar distribution. However, we expect random perturbations of the Teflon-AF coating to randomise the ray paths so that \( 1 \leq k \leq 2 \).

The two equations 3 and 4 multiply to give the fraction of flux transferred from the falling analyte stream to the probe. To find the total flux collected, we introduce a differential flux element \( d\Phi(z) \). This is the photon flux scattered and then collected from a cylindrical differential volume element (cross-section) of thickness \( dz \), at a distance \( z \) from the probe, as shown in figure 2.

Before the emission and collection cone intersects the waveguide wall at \( z_c \), the waveguide has no effect on the amount of flux collected. Beyond the point \( z_c \) the total irradiance on the waveguide cross section is constant, assuming that no light is absorbed. By reciprocity, the flux collected by the probe from any cross section, \( d\Phi(z) \), must also be constant beyond \( z_c \). For the general case where the sample is absorbing, \( d\Phi(z) \) is a function of \( z \), and is given by equation 5.

\[
\begin{align*}
    d\Phi(z) &= P_0 n_o \sigma \exp\left(-\left(\alpha_{\text{ex}} + \alpha_{\text{em}}\right)z\right) S \ L_{\text{NA}} \ L_{\text{radius}} \ dz \\
    &= P_0 n_o \sigma \exp\left(-\left(\alpha_{\text{ex}} + \alpha_{\text{em}}\right)z\right) \sin^2(\omega_{\text{input}}/2) \frac{a^k}{R^k} \ dz \\
\end{align*}
\]

(5)

Here \( P_0 \) is the total flux emitted from the probe tip, \( n_o \) is the number density of scattering molecules, and \( \sigma \) is the total scattering cross section in the direction of collection. The variables \( \alpha_{\text{ex}} \) and \( \alpha_{\text{em}} \) are the absorption coefficients at the excitation and emission wavelengths respectively. If \( \alpha_{\text{ex}} \) and \( \alpha_{\text{em}} \) are both small, then we can expect \( d\Phi \) to be approximately constant. Equations 3-5 are only valid for \( z > z_c \); before this point the flux collected by the probe is unaffected by the presence of the waveguide.

By integrating the flux excited and then collected along a waveguide of length \( z_c \), the expression for the total flux collected, \( \Phi(z_c) \), is given by equation 6.

\[
\begin{align*}
    \Phi(z_c) &= \int_{z_c}^{z_c} d\Phi(z) \ dz + \Phi_{BP}(z_c) \\
    &= \sin^2(\omega_{\text{input}}/2) \frac{a^k}{R^k} \int_{z_c}^{z_c} \frac{P_0 n_o \sigma}{\alpha_{\text{ex}} + \alpha_{\text{em}}} \left\{ \exp\left(-\left(\alpha_{\text{ex}} + \alpha_{\text{em}}\right)z_c\right) - \exp\left(-\left(\alpha_{\text{ex}} + \alpha_{\text{em}}\right)z_c\right) \right\} + \Phi_{BP}(z_c) \\
\end{align*}
\]

(6)

The constant \( \Phi_{BP}(z_c) \) is the flux collected by the probe between \( z=0 \) and \( z=z_c \) (unaffected by the waveguide). If the waveguide is long (large \( z_c \), or narrow (small \( z_c \)) \( \Phi_{BP}(z_c) \) may be ignored. In this work we have presented our results in
terms of the enhancement factor $N$, which is the ratio of the intensity measured by the probe coupled with the waveguide, $\Phi(z)$, to that measured using the probe alone, $\Phi_{pr}(\infty)$. $N(z)$ shares the same dependance on the waveguide parameters as $\Phi(z)$. From equation 6 we see that when $\Phi_{pr}(z)$ is negligible the flux collected, and hence the enhancement $N$, is proportional to $R^4$.

### 2.2 Teflon AF as a waveguide cladding material

Although Snell’s law defines the critical angle for total internal reflection, energy penetrates the waveguide cladding as an evanescent wave, of intensity decaying exponentially with depth. For efficient waveguiding the thickness $t$ of the AF layer should be larger than the penetration depth $\delta$ of the light incident onto the tube wall from the core. This depth is given by equation 7, where $n_i$ is the refractive index of the cladding (AF film), $n_i$ is the refractive index of the liquid core, and $\lambda$ is the wavelength of the incident light.

\[
\delta = \left( \frac{2\pi}{\lambda} \sqrt{\frac{\sin^2(\theta_c)}{(n/n_i)^2 - 1}} \right)^{-1}
\]  

(7)

We have assumed that all energy which penetrates the AF coating is lost from the waveguide. The transmission of rays at an angle $\theta_c$ to the normal of the waveguide wall is then given by equation 8, where $L$ is the length of the waveguide, and $R$ is the waveguide radius. The exponent is the number of reflections that a ray undergoes in the length $L$. Rays incident on the tube wall at angles close to the critical angle are poorly guided, due to their greater penetration depth and the larger number of reflections which they undergo.

\[
T = \exp\left(-\frac{\tan(90^\circ - \theta_c) \cdot L}{2R}\right)
\]

(8)

In figure 3 we have plotted the total transmission through the tube (averaged over all guided ray angles). It is seen that once the rays close to the critical angle have left the waveguide, then the transmission levels off. Analyte absorption has been ignored here, but may be significant, depending on the liquid under study, and the excitation wavelength. It is apparent that, for transmission of greater than 90% through the waveguide, a film thickness of at least 15 µm is required. We aimed to fabricate coatings of at least this thickness in this work.
Figure 3 The calculated total transmission through a liquid cored, AF-1600 clad waveguide vs. length, assuming that at \( L = 0 \) light is isotropically distributed over the numerical aperture of the waveguide, and there are no skew rays. The liquid core is assumed to have a refractive index of 1.33, and have no absorption.

3. DEPOSITION PROCEDURE

Teflon AF-1600 was available to us as a 6% solution in FluorInert FC75. By depositing a known volume of this solution into the PTFE tubes that we wished to coat, and assuming that the solution disperses evenly along the inside of the tube, the thickness of the resulting layer can be calculated. To coat a layer of AF, of thickness \( t \), onto the inside of a tube of radius \( R \), a fraction \( F \) of the internal tube volume must be filled with the AF solution, where \( F \) is given by equation 9.

\[
F = \frac{2\cdot t}{0.06\cdot r}
\]

The tubes coated in this work were available with internal radii of 0.445 mm and 0.955 mm. This required that they be 125% and 52% filled respectively. Two different deposition techniques were investigated, and the films were deposited in layers, with the tubes approximately 20% - 50% filled at a time.

Figure 4 The apparatus used to coat the short tubes.

In our initial experiments, 0.955 mm internal radius tubes, with lengths of up to 200 mm, were internally coated at 20°C with single-layer 15 \( \mu \)m-thick films of AF-1600. Tubes of radius 0.445 mm were coated with two layers by similar process. A known quantity of the AF solution was pumped into the tube using a glass syringe, and the tube was suspended and rotated in a vertical plane, as shown in figure 4. By manually varying the speed of rotation, the bead of solution was made to travel to within 10 mm of each end of the tube. After 1-2 hours the tube could be left rotating at a constant speed (usually between 1/20 and 1/5 of a revolution per second), and the speed adjusted hourly.
until the solution dispersed itself along the tube and the solvent had evaporated. After 24 hours drying at room temperature, the tubes were then placed into an oven at 120°C (10°C above the FC75 solvent boiling point) for 3-12 hours, baked at 180°C (15°C above the AF-1600 glass transition temperature) for a further 3-12 hours, and finally baked for 15 minutes at 330°C (10°C below the temperature at which the AF-1600 begins to decompose). The tubes were then removed from the oven, and a waste section, of approximately 20 mm of tube, was cut from each end and discarded.

Longer tubes of up to 1 m in length had to be coated by a different process, using a thin-walled glass tube as a heater, illustrated in figure 5, to speed evaporation of the solvent. Resistance wire was wrapped around the glass tube with a pitch of approximately 30 mm, and heated the PTFE tubes within it to between 30°C and 35°C. The AF-solution was deposited into one end of the PTFE tubes using a syringe, and then sucked through to the opposite end using another syringe which slipped over the PTFE tube. Typically, before the solution reached the far end of the tube it had spread evenly on the inside wall of the PTFE tube, which was then rotated at approximately 1/6 revolutions per second. Occasionally, beads of solution formed within the tube, so these were dispersed by sucking them back and forth using a syringe. This was repeated until no more beads formed (after approximately an hour for the 0.445 mm radius tubes, up to 24 hours for the 0.955 mm tubes), and then the tube was left rotating in the heater for 5-12 hours.

4. EXPERIMENTAL MEASUREMENTS AND RESULTS

Two experiments are described here. The first was to quantify the performance of the cells as optical waveguides, and the second was to evaluate their utility as spectroscopic cells, where they were used to enhance the collection of fluorescence from a 30 µg/L solution of Panacryl Blue 5G (330%).

4.1. Cell transmission and numerical aperture

The PTFE tubes were then placed into an oven and baked as described previously for the shorter tubes, but without the final 330°C bake, as the tube had to be coiled tightly in the oven, and retained the coiled shape when removed. Approximately 40 mm was discarded from each end of the tubes.

![Figure 5](image-url) A schematic diagram of the heater used to coat the long tubes.

The arrangement illustrated in figure 6 was used to measure the transmission of the water- or fluorescent-dye-cored waveguides. They were filled with liquid using a syringe, and the liquid remained within the tube, held by surface tension. Light from a 674 nm diode laser was coupled into the aqueous core via a 400 µm core, 0.22 NA, optical fibre.
inserted up to 60 mm into one end. A similar fibre was inserted into the other end of the tube, which was coupled to a calibrated optical power meter.

The optical fibres were Heraeus low OH silica, with an NA of 0.22, core diameter of 400 µm, cladding diameter of 440 µm, and a total diameter (including an acrylate buffer) of 650 µm. The laser coupling optics filled the NA of the fibre. When studying the 0.955 mm radius waveguides a section of approximately 40 mm at the tip of each fibre was sleeved with the smaller radius PTFE tube, to keep the fibres close to the centre of the waveguide.

4.2. Fluorescence collection enhancement

A similar arrangement was used to measure the fluorescent enhancement due to the use of the waveguides, illustrated in figure 7. First, the intensity of fluorescence collected by immersing the fibre probe directly into the fluorescent dye was measured. Then, the waveguides were filled with the fluorescent dye solution, and the probe inserted into the aqueous core. Excitation light at 674 nm, and scattered light, was coupled to and from the probe via a 50:50 coupler. The scattered light was resolved using a concave-grating CCD-spectrograph.

**Figure 7** Measuring the fluorescence intensity of light collected using a bare optical fibre probe, and with the probe sheathed in an internally-Teflon-AF-coated PTFE tube. The length \( L \) was varied.

4.3. Transmission and fluorescence collection results

In this section we present the transmission and fluorescent collection enhancements of the waveguides. First we present the results for the shorter (less than 200 mm) waveguides, and then the results for the longer (greater than 800 mm) waveguides are given.

4.3.1 Optical transmission of the water filled tubes

The graphs in this section show the optical power collected from water- and dye-solution-cored waveguides in transmissive mode. The total apparent absorption (\( \alpha / \text{mm} \)) has been calculated in each case from the slopes of the regression lines shown, and its value is given (inset) in each graph. These transmission measurements were made at a wavelength of 674 nm, where the absorption of water is \( 0.02 \times 10^{-3} \text{ mm}^{-1} \), and the absorption of the 30 µg/L Panacryl Blue solution is \( 0.149 \times 10^{-3} \text{ mm}^{-1} \). These values are seen to be insignificant compared with the loss of the waveguides themselves.
Figure 8 The optical transmission through the short AF-1600 coated water- and dye-solution-filled waveguides, compared with a section of uncoated tube; a) 0.445 mm internal radius b) 0.955 mm internal radius.

Figure 9 The optical transmission through the long AF-1600 coated water- and dye-filled waveguides, compared with a section of uncoated tube; a) 0.445 mm internal radius b) 0.955 mm internal radius

Variations in the level of side scattering from the long tube were clearly visible, probably due to variations in the AF film thickness.

4.3.2 Fluorescent collection enhancement using waveguiding cells

In this section we have presented the enhancement in the collection efficiency of a single optical fibre probe when coupled with the waveguiding cells, as shown in figure 7.
Figure 10 The fluorescent collection enhancement from coupling a single optical fibre probe with the short AF-1600 coated waveguides. a) 0.445 mm internal radius b) 0.955 mm internal radius.

Figure 11 The fluorescent collection enhancement from coupling a single optical fibre probe with the long AF-1600 coated waveguides. a) 0.445 mm internal radius b) 0.955 mm internal radius.

The effects of variations in the film thickness are evident here in the large and rapid changes in collection enhancement, especially in figure 11. The collection efficiency was only reasonable when the probe tip was sheathed in a strongly guiding part of the cell. Other poorly-guiding regions were found to prevent the enhancement increasing linearly with length, as expected by theory.

Throughout the experiments the movement of the optical fibre against the cell walls did not cause any visible damage to the AF films. In addition, immersion for several days in water and IPA did not affect the adhesion of the films to the PTFE wall.
5. CONCLUSIONS

We have shown that the Teflon-AF fluoropolymer forms a flexible and stable layer when deposited onto a PTFE substrate. In addition, we have modelled and demonstrated the use of such a structure to enhance the light collection efficiency from a fluorescent emission measurement. The technique is equally suited to measurement of Raman light emission, and as we have shown, it is convenient to couple the cell to an optical fibre probe. We have measured a maximum signal enhancement of 3 times in this work, but we expect much larger enhancements if better surface quality could be obtained.

The large scatter of the measured data away from the expected regression lines, due to surface roughness of the AF film, and variations in the film thickness, has resulted in poorer than expected enhancement of the fluorescent collection efficiency. The tube which displayed the best waveguiding and most linear increase in enhancement with cell length, the short 0.955 mm internal radius tube, was the only tube to be coated in one layer, and this may be a pointer towards a better fabrication process. In any case, there is a need to develop a more repeatable coating process.

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