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Polyvinylidene Fluoride Coated Optical Fibre for Detecting Perfluorinated Chemicals

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Abstract: This work reports the development of a Fabry-Perot Interferometry (FPI) based optical fibre to detect perfluorooctanoic acid (PFOA) and other perfluoroalkyl substances (PFAS) in aqueous solutions. A novel and simple sensor fabrication procedure utilizing an immersion precipitation-based phase inversion process to form a thin polyvinylidene fluoride (PVDF) coating at the end-faces of freshly cleaved optical fibres is presented. The PVDF coating was rich in the electroactive β -phase, which enhances dipole-dipole and hydrophobic interaction with PFAS at binding sites. Sensor testing with model PFOA solutions showed that the PVDF coated FPI optical fibre can detect PFOA. The change in optical path difference (OPD) with change in PFOA concentration was considered as a measure of sensitivity and it corresponded to a value of 0.9 to 5 nm/ppm for PFOA. In real PFAS solutions obtained from fire-fighting foams, this value was found to be significantly more sensitive at 178 nm/ppb.

Keywords: perfluorooctanoic acid; perfluoroalkyl substances; optical fiber sensors; Fabry-Perot interferometry; polyvinylidene fluoride

1 Introduction

Contamination of water and land by perfluoroalkyl substances (PFAS) has been reported in many parts of the world in recent years [1, 2]. The discovery of organic fluorochemicals in human serum and the environment has initiated growing interest in characterising the effects and the extent of their presence in the environment [3-5]. Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate, and perfluorononanoic acid are among the common forms of PFAS which have been studied extensively [6, 7]. They are commonly found in surfactants, aerosol propellants, insecticide, refrigerants, anaesthetics, and plastics [8] and are used in the production of non-stick cookware, food packaging, fire-fighting foams, and some water and oil proof fabrics [9, 10]. Recent reports show that locations of PFAS contaminated land, ground water or reservoir are usually close to manufacturing plants [11], or

33 near military bases [12], airports and firefighters' training grounds [13]. Many of these have a
34 history of using a specific fire retardant, namely aqueous film-forming foam (AFFF) [13, 14].
35 The fluorinated components present in AFFF, typically PFOA and PFOS, are dispersed during
36 military or fire training exercises or during actual fire extinguishing events and are suspected
37 to be the cause of the environmental pollution.

38 Due to the inherent strength of the C-F bond, PFAS do not readily biodegrade and are known
39 to accumulate once released into the environment [15] which can present a health risk to
40 humans and animals who may consume PFAS contaminated food or water. It has been reported
41 that PFAS may adversely affect foetal growth and learning behaviour in children, decrease
42 fertility, increase cholesterol, cause hormone dysfunction, affect the immune system, and
43 increase the risk of cancer [15]. Several studies on a population exposed to very high levels of
44 PFOA have suggested that it strongly correlates to various diseases including kidney and
45 testicular cancer, ulcerative colitis, thyroid disease, hypertension and high cholesterol [16].
46 Both PFOA and PFOS are listed in the Stockholm Convention on Persistent Organic Pollutants,
47 which prohibits their production and the import or export of foams containing either or both
48 chemicals in more than 180 countries [17].

49 Environment Protection Agencies or equivalents around the globe have expressed the need to
50 monitor these contaminants, while addressing issues regarding regulation and development of
51 adaptive frameworks like the National Environment Management Plan (NEMP) [18] to
52 respond to emerging research and knowledge. Based on scientific reports and evidence, Food
53 Standards Australia New Zealand (FSANZ) has considered 0.56 to 5 ppb of PFOA and
54 0.07 ppb of PFOS in drinking water to be the maximum safe level for human consumption
55 [19]. The tolerable daily intake values for PFAS, including PFOS and PFOA, recommended
56 by FSANZ is 160 nanograms per kilogram of body weight per day [20].

57 Current detection methods for PFOA and PFOS contaminants in water are based on
58 conventional techniques such as liquid chromatography coupled with mass spectrometry (MS)
59 or tandem MS [21, 22] or gas chromatography coupled with MS [23]. These are all costly and
60 time-consuming processes that often require complicated pre-treatment steps, expensive labour
61 resources, and are inapplicable for *in situ* measurements and analysis [7]. Molecularly
62 imprinted polymer-based portable sensors have been proposed to address this issue, but they
63 are unable to differentiate between different types of PFAS and require long fabrication times
64 [24-26]. A smartphone-based system developed recently as a portable PFAS detector is

65 susceptible to variation in weather conditions [24]. In addition, there is a lack of information
 66 regarding the effect of temperature on sensitivity of these portable sensors, their cross-
 67 sensitivity to other contaminants, and in some cases the generation of toxic wastes. There is a
 68 clear need for robust, portable sensing systems that can be used in the field and fibre optic
 69 sensors may be suitable for this application due to their many inherent advantages. Optical fibre
 70 sensors (OFS) are known for their small size, immunity to electromagnetic interference,
 71 passiveness and intrinsic safety, high sensitivity and bandwidth, multiplexing capability,
 72 chemical inertness, and robustness to hostile environments. Additionally, sensors based on
 73 optical fibres are suitable for remote sensing operations and are compatible with online
 74 continuous monitoring applications. As the technology is portable [27], it can be easily
 75 configured to provide real time information on any physical, chemical or biological measurand
 76 in a field test. More importantly, chemical sensing functionality of OFS can be further
 77 enhanced by coating chemically selective optical materials at the end-face of optical fibres as
 78 in Fabry–Perot interferometric (FPI) fibre optic sensors. A comparison between the
 79 conventional methods of PFAS analysis and/or detection and FPI based OFS is provided in
 80 Table 1.

81 **Table 1 Summary of current PFAS analysis and detection methods.**

Technique	Advantages	Disadvantages	References
GC-MS LC-MS	<ul style="list-style-type: none"> ▪ High accuracy ▪ Good selectivity and reliability ▪ Limit of detection is in ppt range 	<ul style="list-style-type: none"> ▪ Time consuming preparation steps ▪ Requires bulky instruments ▪ Requires trained personnel ▪ Non-portable ▪ Complex data analysis technique ▪ Expensive 	[28-32]
Smart-phone colorimetric analysis	<ul style="list-style-type: none"> ▪ Portability, field application ▪ Rapid analysis ▪ Readily available kit 	<ul style="list-style-type: none"> ▪ Not selective to PFAS, can detect other surfactants ▪ Low detection limit ▪ Toxic chemicals needed ▪ Toxic waste generated 	[24]
FPI based OFS	<ul style="list-style-type: none"> ▪ Portability, field application ▪ Convenient and economic ▪ Can be used for remote sensing and real time continuous monitoring options ▪ Easily optimized ▪ Light weight 	<ul style="list-style-type: none"> ▪ Susceptible to temperature variation ▪ Stabilizes slowly in aqueous solution ▪ Functionalization procedures are time consuming ▪ Sensitivity is subject to functionalization ▪ Limit of detection is in ppm range 	[33-35]

82

83 Fabry–Perot interferometric fibre optic sensors have been demonstrated for monitoring
84 humidity [36, 37], acoustic wave intensity [38], magnetic fields [39], mechanical vibrations
85 [40], marine phosphate [41] and temperature [42, 43]. Most of these FPI sensors are analogous
86 to an optically transparent material with two mirror-like surfaces, whereby the distance or
87 refractive index between the surfaces can vary to bring about changes in path difference of
88 reflected light beams. Generally, FPI sensor fabrication techniques reported in literature
89 include processes such as chemical or physical vapour deposition [44, 45], laser
90 micromachining [46], ionic self-assembly monolayer process (ISAM) [47], splicing [48] and
91 dip coating [49]. Among these fabrication methods, etching or laser micromachining involve
92 hazardous and complex protocol, whereas others, such as the ones that form the FPI sensors
93 from two separate fibres bonded through the use of an external casing [50] or splicing [42],
94 cause excessive coupling loss or low reflectivity issues in the end product.

95 The ability to detect contaminants in water using FPI relies on the affinity of the contaminant
96 for the coating on the end of the fibre to induce a signal. Polyvinylidene fluoride (PVDF) is a
97 hydrophobic polymer that has widespread usage in water treatment facilities and can be easily
98 functionalized and processed to form thin films using phase inversion [51-53]. Utilizing a
99 PVDF coating on the sensor can utilize the polymer's ferroelectric properties due to the
100 presence of the beta (β) or gamma (γ) phase in the polymer structure. The surface charge on
101 PVDF can help in binding with PFOA in aqueous solution through dipole-dipole or
102 hydrophobic interactions, since the contaminant has a carboxylate group that interacts strongly
103 with polar substances and also an octyl group, which is inert and hydrophobic. A recent study
104 has provided further evidence that PVDF is compatible for use with optical fibre sensors, that
105 offers numerous advantages over conventional electrical or electrochemical sensors including
106 portability, remote sensing and real time monitoring in underground wells and bore holes [33].

107 In this work, we report the development and testing of a PVDF coated FPI fibre optic sensor
108 for detecting PFAS in aqueous solutions. The PVDF coating, developed using a phase inversion
109 process based on a freshly cleaved end-face of a standard telecommunication grade single mode
110 optical fibre, was tested in model PFOA solutions followed by real AFFF solutions. The
111 potential for sensitivity to temperature variations was also performed. To the best of our
112 knowledge, this is the first report of PFAS detection by PVDF coated optical fibre. Moreover,
113 there are no other reports of forming a PVDF coating at the end-face of an optical fibre using
114 the method described herein.

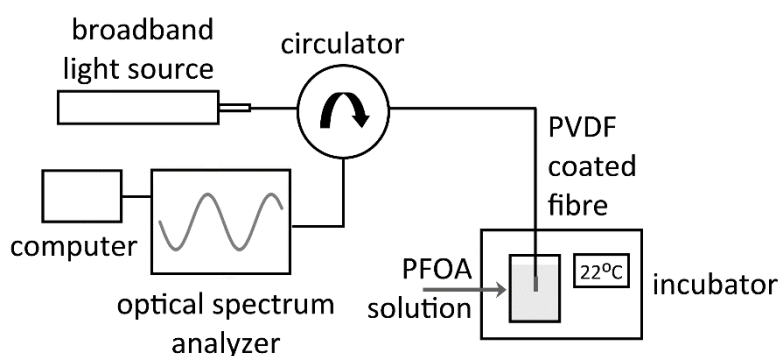
115 **2 Materials and Methods**

116 **2.1 Materials**

117 The PVDF polymer used was Solef 1015 obtained as a powder from Solvay (Australia).
118 Solvents *N,N*-dimethylformamide (DMF), polyvinyl butyral (butvar) and chloroform were
119 obtained from Sigma-Aldrich (Australia). The PFOA with a purity of 95% was also purchased
120 from Sigma-Aldrich (Australia). A sample of AFFF was obtained as a diluted solution and was
121 analysed by an external laboratory for its composition (see Table S1 in Supplementary
122 Material). Ultrapure (Milli Q) water was used throughout the experiments and no chemical
123 reagent was modified prior to its usage.

124 **2.2 Optical Spectrum Analyzer Setup**

125 The experimental setup incorporating the optical fibre sensor for determining the PFOA
126 concentration consisted of an ANDO AQ6317B Optical Spectrum Analyzer (OSA), an Erbium
127 Broadband Source (EBS) from MPB Communications Inc. and a three-port optical circulator
128 as shown in the schematic Figure 1. It also included a ThermoScientific table-top incubator for
129 maintaining a constant environmental temperature surrounding the sensor probe. Temperature
130 readings were acquired using a K-type thermocouple connected to a Fluke 52 II electronic
131 thermometer.



132

133 Figure 1. Schematic of the experimental setup

134 For data acquisition purposes, the OSA resolution was set at 0.1 nm and the centre wavelength
135 at 1565 nm with a span of 11 nm. The sampling rate was set at 1001 points over the
136 1520-1610 nm wavelength range. Automated continuous data acquisition was achieved
137 through a GPIB card and LabVIEW interface, while further data analysis of the recorded
138 spectral information was performed using MATLAB and Microsoft Excel. A photograph of
139 the actual apparatus is presented in the Supplementary Material (Figure S1).

140 **2.3 Optical Fibre Coating**

141 The PVDF coating solution was formed by heating 1.67 g of PVDF powder in 14 mL of DMF
142 at 80 °C for 1 h under constant stirring. To promote good adhesion between the optical fibre
143 glass and PVDF, 0.03 g of the cross-linking agent Butvar was first dissolved in 2 mL of
144 chloroform and then added to the homogenous PVDF solution mixture at 80 °C and mixed
145 thoroughly with a stirrer to avoid agglomeration. The solution was allowed to cool to room
146 temperature. Stripped, cleaned and cleaved optical fibres were manually dipped vertically into
147 the PVDF solution for 5-10 s and to a depth of 1-2 cm at room temperature and were then
148 immersed vertically into a beaker containing ultrapure water for 10-20 s to induce coagulation
149 and develop the coating. To obtain a satisfactory thickness of the thin film on the fibre end-
150 face, the dipping procedure was repeated while allowing enough time for a coated layer to dry
151 in between subsequent intervals. Similar PVDF films were obtained by dip coating glass slides
152 in the solution for characterization. A flow diagram of the dipping procedure is presented in
153 the Supplementary Material (Figure S2).

154 **2.4 Coating Characterization**

155 A Perkin-Elmer Frontier Fourier-transform infrared (FTIR) spectrophotometer with a diamond
156 attenuated total reflectance (ATR) crystal was used for characterization of the PVDF coating
157 and identifying its phase composition. Film samples were cast on glass slides in accordance
158 with the method described in section 2.3, were peeled from the slide then clamped onto the
159 ATR crystal. A minimum of 32 scans were performed over the wavenumber range 4000-650
160 cm^{-1} with a minimum of 5 samples averaged. A Hitachi TM3030 Plus Tabletop SEM using an
161 accelerating voltage of 15 kV in backscattering mode was used for obtaining images of the
162 PVDF coatings on optical fibre end faces. Samples were coated with iridium prior to obtaining
163 the images.

164 **2.5 Quantification of PFOA Adsorption**

165 A sample of 1 mg/L PFOA solution was prepared and a section of PVDF film was soaked for
166 several hours. Samples of the PFOA solution before and after soaking in PVDF were sent to
167 ALS Water (Scoresby Victoria) where they were subjected to quantitative analysis in
168 accordance with NATA accredited ALS Method EP231X.

169 **2.6 Sensor Selection**

170 The raw spectral data obtained from a PVDF coated optical fibre, using the experimental set
171 up shown in Figure 1, were normalized against the reflection spectrum of a cleaved fibre end-
172 face taken before splicing the sensor to the system. A normalized spectrum, free of source
173 modulation effects that showed a sinusoidal curve was considered an indication of a good
174 sensor from the perspective of data analysis. Only coated fibres that displayed such
175 characteristics in their normalized spectra were selected for further experimentation.

176 **2.7 Measurement of Temperature Response**

177 The experimental setup shown in Figure 1 was used to determine the sensitivity of the PVDF
178 coated fibre to variations in temperature in water. The incubator thermostat setting was changed
179 to vary the temperature of water in which the PVDF coated fibre was submerged and
180 maintained until the temperature of the water stabilized to that value and data acquisition was
181 completed. The PVDF coated fibre was first stabilized at a temperature close to the room
182 temperature for several hours and then subjected to the actual temperature variation test. The
183 temperature was then increased or decreased in steps of 10 °C between 22 to 60 °C and
184 measurements at specific intervals were taken when the coated fibre had stabilized and the
185 temperature reading on the thermometer was steady.

186 **2.8 Measurement of Response to PFOA**

187 A 100 ppm PFOA stock solution was prepared by dissolving 0.01 g of PFOA in 100 mL of
188 ultrapure water under heating at 80 °C for 10 minutes. Test solutions of concentrations ranging
189 between 10 to 60 ppm were obtained by diluting the stock solution. The PVDF coated fibre
190 was stabilized in 20 mL of ultrapure water at a temperature of 23.8 °C and data acquisition was
191 performed using the setup shown in Figure 1. After stabilization, a known volume of the PFOA
192 stock solution was added to the submerged PVDF coated fibre to form a desired concentration
193 and data acquisition was performed following stabilization in the PFOA solution. The addition
194 of PFOA, stabilization and data acquisition were repeated until all the spectral information at
195 different concentrations of PFOA were obtained.

196 **2.9 Measurement of Response to AFFF Solution**

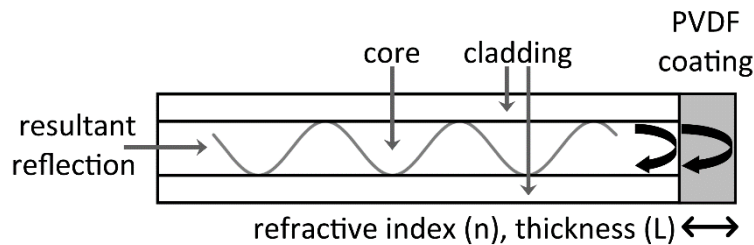
197 A sample of diluted AFFF with known concentrations of PFAS was used in this test. The
198 solution was comprised of different PFAS compounds as shown in the Supplementary Material
199 (Table S1) and was confirmed to contain a total of 1.14 ppb of total PFAS. The steps used to

200 measure the response to different concentrations of the AFFF were the same as those presented
 201 in section 2.8.

202 3 Results and Discussion

203 3.1 Sensor Description and Operating Principle

204 Figure 2 shows a schematic of the low finesse PVDF coated fibre formed by dip coating and
 205 immersion precipitation. The PVDF coating acts as a Fabry-Perot (FP) etalon that reflects light
 206 from the two interfaces as shown in Figure 2. The reflected light waves interfere to produce a
 207 resultant reflection spectrum, which is sensitive to changes in the PVDF coating's physical
 208 thickness, refractive index or both. A change in PFOA or PFAS concentration brings about a
 209 change in the thickness of the PVDF coating due to molecular interaction and attachment of
 210 the analyte to the surface of the thin film. This in turn causes a phase difference between the
 211 reflected beams from the inner and outer surface of the FP etalon by altering the optical path
 212 difference (OPD) between them and leads to the resultant interferogram being shifted. In the
 213 experiments, the wavelength shift in the spectrum was monitored in real time using the OSA
 214 and the variation in OPD with analyte concentration change was measured after data
 215 acquisition to determine sensor performance.



216

217 Figure 2. Schematic of PVDF coated optical fibre

218 Equation (1), represents an expression of the overall reflected light intensity from the FPI
 219 sensor for a two-beam interference model. This was used to simulate the normalized reflection
 220 spectra and curve fitting to determine OPD from the coefficient of fitted curves.

$$I = I_1 + I_2 + 2\gamma\sqrt{I_1I_2} \cos\left(\frac{4\pi nL}{\lambda} + \phi_0\right) \quad (1)$$

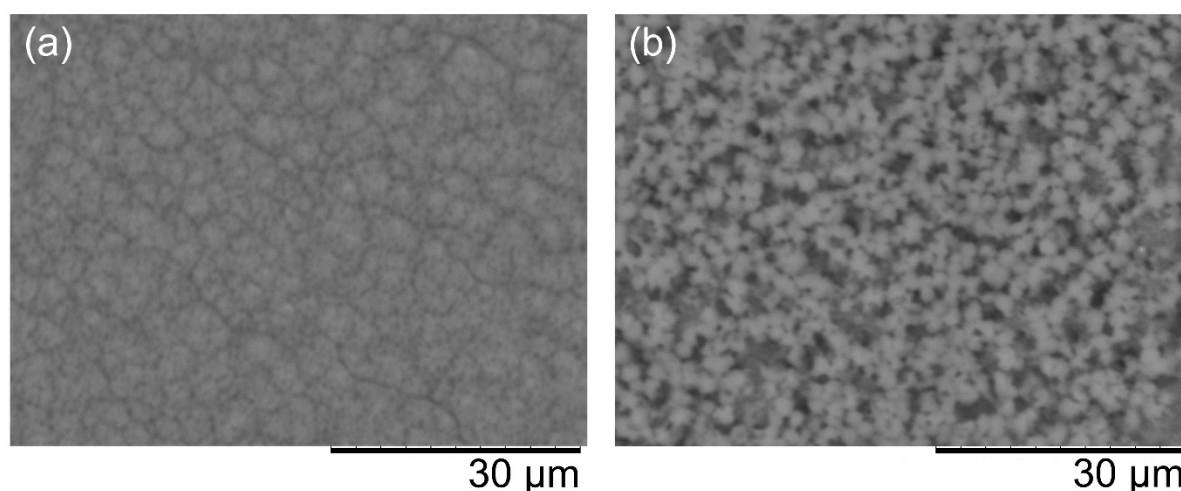
221 Here, I_1 and I_2 and are the intensities of the reflected rays from the PVDF coating's inner and
 222 outer boundaries, γ is the degree of coherence, ϕ_0 is the initial phase difference of the reflected
 223 intensities, λ is the wavelength of light in free-space, and n and L are the refractive index and

224 thickness of the PVDF thin film respectively. The product of n and L is the OPD which was
225 determined by curve fitting techniques and used as a measure of sensitivity in this work.

226 Mathematical modelling with equation (1) has shown that varying the initial thin film thickness
227 (L) affects the number of peaks and troughs present in an interferogram as well as their
228 positions on an intensity versus wavelength graph. This can have implications from a data
229 acquisition or analysis point of view, which alludes to the fact that an interferogram with the
230 necessary combination of peaks/troughs generated for monitoring should be within the
231 available spectral window formed by the combination of the EDFA broadband source and
232 optical spectrum analyzer used in the experimental arrangement for this work.

233 3.2 Characterization of PVDF Coating and PFOA Adsorption

234 The FTIR spectra of a typical PVDF film depicts characteristic peaks at 840 and 1275 cm^{-1}
235 [54] which are representative of the electroactive β -phase of PVDF (see Figure S3 in the
236 Supplementary Material). This supports the presence of surface charge on the PVDF coating
237 which has been considered to play an important role in selectively attracting the PFOA
238 molecules in solution to the binding sites on the coating. Analysis of PFOA concentrations
239 before and after PVDF film immersion confirmed that *ca.* 10% of PFOA was adsorbed on to
240 the PVDF film. Furthermore, the SEM images shown in Figure 3(a) and (b) show differences
241 in the surface morphology of PVDF films before and after exposure to PFOA. The presence of
242 nodule like structures on the surface in Figure 3(b) may be an indication of the clusters/micelles
243 of PFOA reported previously [55] that may have formed due to the hydrophobic or dipole-
244 dipole interaction of PFOA molecules with PVDF.



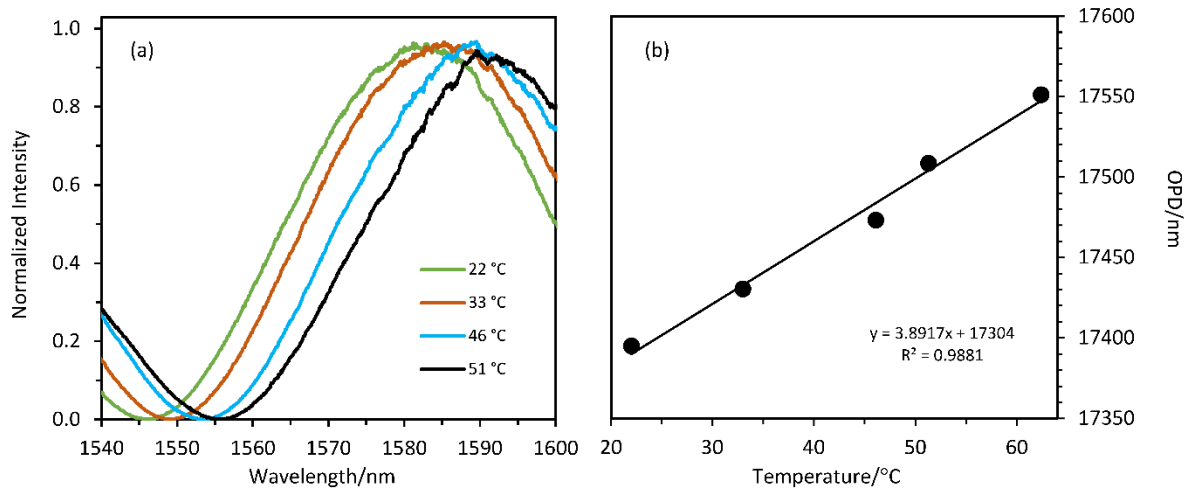
245

246 Figure 3. SEM images of PVDF film surface: (a) before and (b) after immersion in PFOA

247 3.3 Response of Sensor to Temperature Variation

248 The reflection spectra exhibit a redshift or peak wavelength (λ_p) shift towards the higher
249 wavelength region, as shown in Figure 4 (a), with increasing temperature in water. This implies
250 that the changes in OPD are primarily the result of changes in physical thickness due to thermal
251 expansion. There is an added effect of a changed refractive index of the surrounding medium,
252 which creates an impact on the wavelength shift and cause the final spectrum to be different
253 from that in air. The spectral wavelength shift is therefore dependent on the optical thickness
254 which is linked to the characteristics of the ambient medium in the immediate vicinity of the
255 sensor.

256 Both the peak wavelength shift and OPD shown in Figure 4 (a) and (b) exhibit a linear response
257 over the test temperature range of 20-60 °C with a resulting temperature sensitivity of
258 3.9 nm/°C calculated as change in OPD per unit change in temperature. This suggests that,
259 outside of the controlled laboratory set up, the OPD change with temperature variation must be
260 compensated in order to correctly determine the PVDF coated fibre's response to PFOA or
261 other analytes. The issue of temperature cross sensitivity for field sensing applications can be
262 addressed by using a rare earth doped fluorescence intensity ratio based optical fibre
263 temperature sensors [56-58] in conjunction with the PVDF coated fibre. Fluorescence intensity
264 ratio based temperature sensing has been shown to be one of the most successful in the past
265 demonstrating a sensitivity in the order of 1.1 to 1.6% change in the measurand per degree
266 Celsius, which is much higher than that of the FBG ($7 \times 10^{-4} \%$ /°C) [59]. Thus, to eliminate the
267 effect of temperature sensitivity from the PFOA detection test in the present study, experiments
268 with the PVDF coated fibre were performed under constant temperature conditions. The
269 subsequent protocol adopted for performing the sensitivity test of the PVDF coated fibre to the
270 PFOA/PFAS concentrations therefore assumed that the OPD change observed is only due to
271 the change in analyte concentration and not as a result of temperature variation.



272

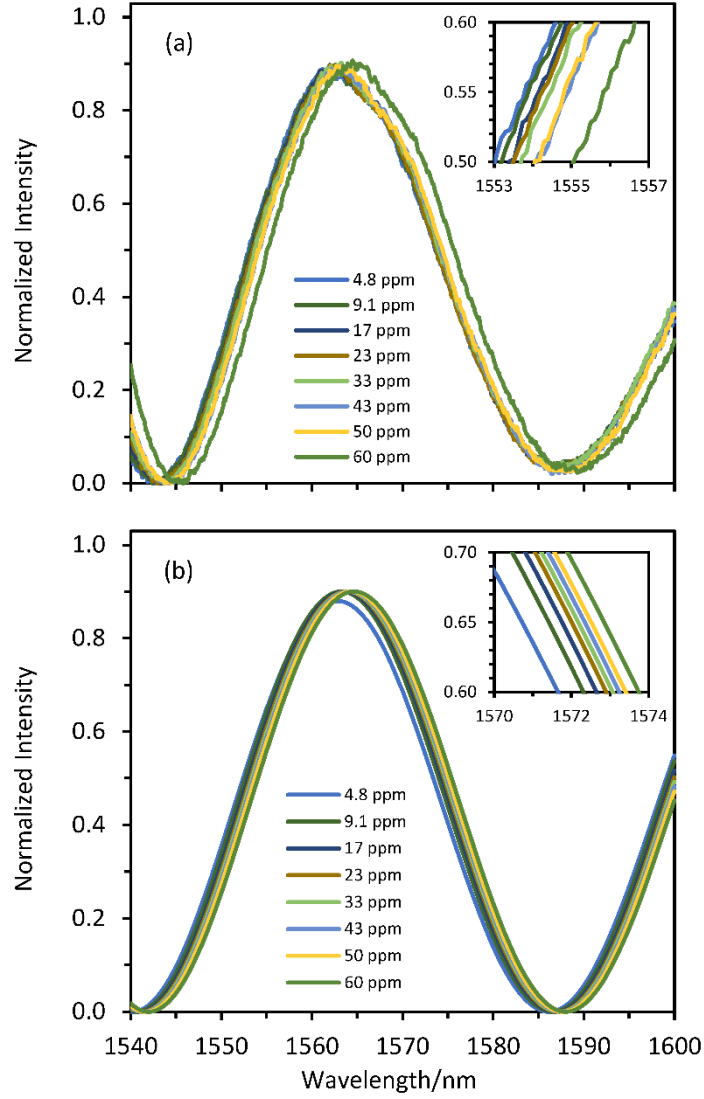
273 Figure 4. Effect of temperature change on: (a) peak wavelength shift in FPI spectra and (b)

274 variation in OPD (color version available online)

275 3.4 Response of Sensor to PFOA

276 The raw sensor spectra obtained for in PFOA solution of different concentrations at a constant
 277 temperature of 23.8 °C is shown in Figure 5 (a). The method of PFOA detection based on FPI
 278 involved observation of wavelength shifts using the setup shown in Figure 1 and the
 279 measurement of OPD from individual fitted spectral data was determined using Excel. Curve
 280 fit parameters generated by the mathematical model given by equation (1) resulted in values of
 281 n and L at specific concentration. Correlation between the normalized spectral response from
 282 the coated fibre and the Excel fits (Figure 5 (b)) were found to be in the order of 0.96~0.99.

283



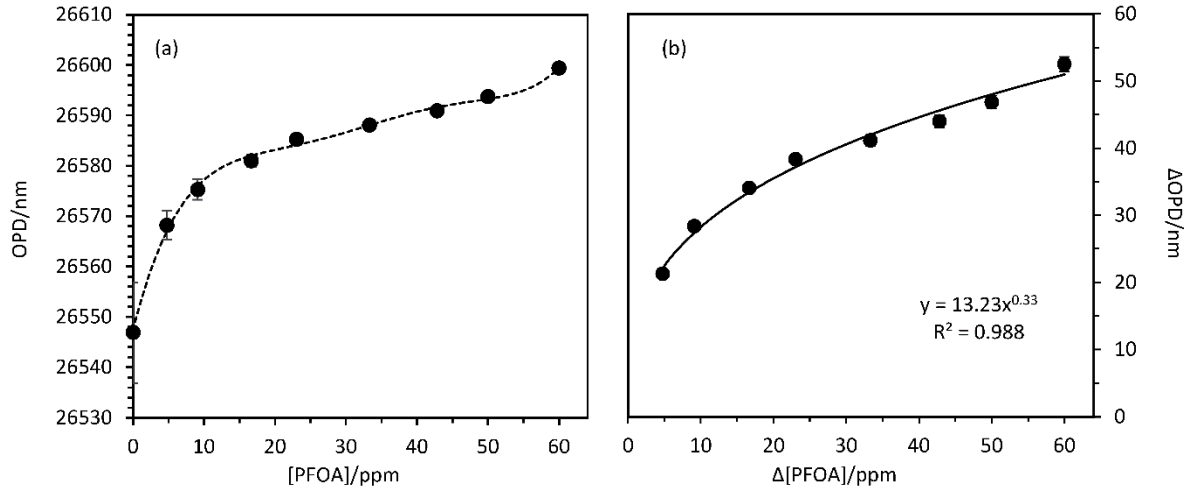
284
 285 Figure 5. Sensor response to change in PFOA concentration: (a) raw data, and (b) fitted
 286 curves (b) where zoomed inlays show increasing concentration left to right from 0 to 60 ppm
 287 (color version available online)

288 Calculations were performed on the actual normalized spectra using equation (2):

$$\left(\frac{4\pi nL}{\lambda_1} + \phi_0\right) - \left(\frac{4\pi nL}{\lambda_2} + \phi_0\right) = 2\pi \quad (2)$$

289 where λ_1 and λ_2 are the wavelengths of the adjacent peaks or troughs. In this case, the expected
 290 value of L was 18333 to 18380 nm over the PFOA concentration range 4.8 and 60 ppm when
 291 the value of n was 1.42.

292 The SEM image of the cross section of a PVDF coated fibre has revealed a coating thickness
 293 ranging between 10-40 μm on the optical fibre (see Figure S4 in the Supplementary Material).
 294 Excel fits rendered the L values 18710 and 18732 nm over the chosen range which falls within
 295 this limit (i.e. 18.7 μm) and the average values was then used for the OPD analysis shown in
 296 Figure 6.



297

298 Figure 6. Effect of PFOA concentration on: (a) OPD, and (b) change in OPD with fitted
 299 equation

300 From the analysis of the OPD plots shown in Figure 6 (a), it was assumed that PFOA adsorption
 301 on the surface of the PVDF membrane increases with increasing concentration of PFOA until
 302 all the binding sites are occupied and the film surface is saturated. The development of a layer
 303 of PFOA is therefore assumed to cause a change in the apparent thickness of the PVDF coating
 304 on the end of the fibre which results in a change in the OPD value. The sensitivity of the coated
 305 fibre was derived from the OPD plot and is nonlinear as shown in Figure 6 (b) with the fit
 306 obtained given by equation (3):

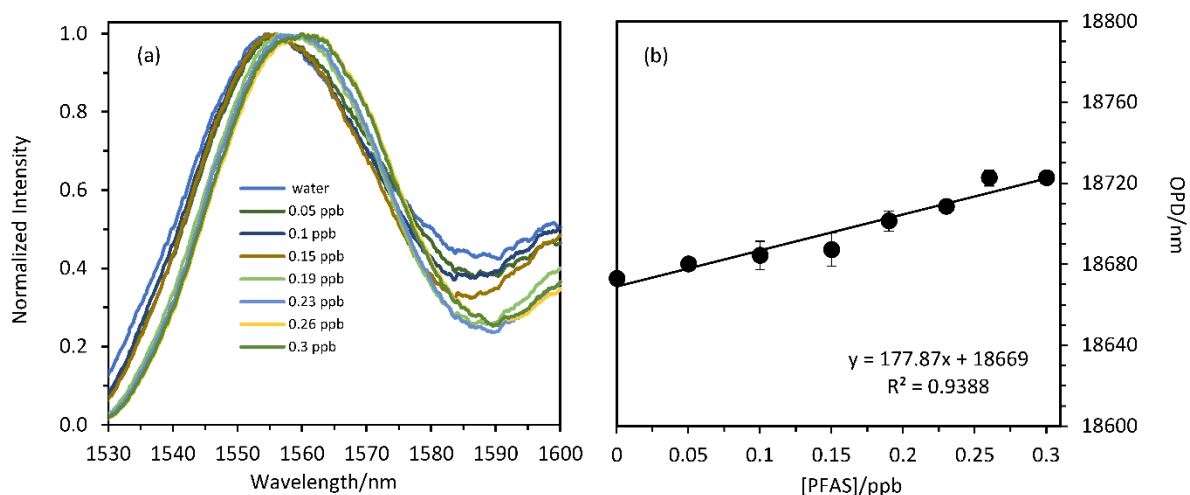
$$\Delta\text{OPD} = 13.23 \times \Delta[\text{PFOA}]^{0.33} \quad (3)$$

307 It was observed that the sensor's sensitivity (i.e. $\Delta\text{OPD} / \Delta[\text{PFOA}]$) varies from approximately
 308 5 nm/ppm to 0.9 nm/ppm over the tested concentration range. The small errors associated with
 309 the measurements (see Figure 6), also suggest a reasonably high level of accuracy within the
 310 measurements. Furthermore, through separate careful experimental procedures carried out
 311 using a range of low PFOA concentrations between 0.1 ppb and 1 ppb, it was observed that the
 312 PVDF coated fibre did not produce significant wavelength shift when the PFOA concentration

313 was below 5 ppm (see Figure S5 in supplementary material). The limit of detection for PFOA
314 concentration was therefore considered to be approximately 5 ppm.

315 **3.5 Response of Sensor to AFFF**

316 The PVDF coated fibre has shown a positive response to the model compound PFOA but at
317 relatively high concentrations. In real samples, the composition of PFAS is more diverse with
318 a range of different compounds at different concentrations. The spectral data obtained for the
319 measurement of the PVDF coated fibre response to AFFF is presented in Figure 7(a), where a
320 sensitivity in the ppb range was obtained. This observation has important implications for
321 further development of the coated fibre as a potential field sensor where real contaminated
322 water sources will have similar compositions to the sample of AFFF solution used in this study.
323 Although the results do not confirm whether the response is derived from a specific compound
324 in the AFFF mixture, it may be used as a screening test to show the presence of general PFAS
325 compounds. From the OPD plot versus concentration in Figure 7(b) the linear fit of the data
326 points suggest a sensitivity of 178 nm/ppb (i.e. OPD change per ppb) of PFAS, which is
327 considerably higher than the PFOA sensitivity mentioned above and sensitivity of other
328 reported sensors [35] within this range of concentrations. Moreover, the low errors associated
329 with the data as depicted by the error bars in Figure 7(b) are an indication of a high level of
330 accuracy associated with the measurements. The response to other PFAS in the ppb range may
331 suggest that the actual limit of detection could be lower and it may be dependent on parameters
332 like surface morphology, availability of binding sites etc., which varied in the case of each
333 individual sensor. It may also suggest that the PVDF is more sensitive to PFOS since the
334 concentration was nearly thirty times higher than PFOA in the AFFF. Further evaluation of the
335 selectivity is therefore required in order to assess the suitability of the PVDF coated fibre to
336 detect these emerging contaminants. The addition of zeolites or other active sites to the PVDF,
337 for example, may enhance the selectivity towards particular AFFF components thereby
338 improving the suitability of the sensor for robust field applications.



339

340 Figure 7. Effect of AFFF concentration on: (a) spectral shift and (b) change in OPD where
 341 zoomed inlay in (a) shows increasing concentration left to right from 0 to 0.3 ppb (color
 342 version available online)

343 4 Conclusions

344 In this study, a novel optical fibre coating system using PVDF was developed, optimized and
 345 tested in order to measure the concentration of PFAS in aqueous solutions. The system, based
 346 on the principle of FPI, was shown to be sensitive to temperature variations although this can
 347 be compensated or corrected accordingly. The PVDF film was shown to effectively adsorb
 348 PFOA from model aqueous solutions. Testing of the sensors in the PFOA solutions showed a
 349 detection sensitivity of 0.9 to 5 nm/ppm. Further testing in real AFFF solutions showed
 350 improved sensitivity of 178 nm/ppb. This work has demonstrated a concept for the future
 351 development of a feasible FPI sensor utilizing a PVDF coating for the field detection of PFAS
 352 in the natural environment.

353 5 Acknowledgements

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356 6 Competing Interests Declaration

357 The authors declare no conflict of interest.

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