# Optical fiber methane sensor using refractometry

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***Abstract*—One potential application of fiber refractometers is gas detection. In this work, a multimode fiber (MMF) refractomer has been designed as a $CH_4$ sensor by de-cladding 2 cm of the MMF and then functionalizing this region using a polymeric thin film of cryptophane-A supramolecules incorporated within a styrene acrylonitrile (SAN) host. $CH_4$ concentration is subsequently measured by observing the variation of the transmitted optical power along the MMF compared to an unfunctionalized MMF used as reference. This variation is induced by the modification of the refractive index of the functionalized film due to $CH_4$ concentration variation. The proposed sensor is potentially of lower cost than alternative sensors and can detect $CH_4$ concentration with a resolution of 186 ppm at a relatively fast response of ~25 s.**

***Keywords—Fiber refractometer; methane sensor; multimode fiber; cryptophane-A; styrene acrylonitrile***

## I. INTRODUCTION

Methane ($CH_4$) sensors continue to attract intense interest since it is one of the most important greenhouse gases (GHG). Although second only to carbon dioxide ($CO_2$) in terms of emission, $CH_4$ strongly absorbs in the infrared spectrum and has a global warming potential 25 times stronger than that of $CO_2$ [1,2]. As reported by the United States Environmental Protection Agency, $CH_4$ emission is estimated at 10% of total GHG emissions, rendering it the second largest GHG emitted by the USA by volume [3]. Globally, however, the contribution from $CH_4$ is even higher, estimated at between 15-20% [1].

With $CH_4$ playing such a critical role in global warming, an intensive global monitoring and study effort thus needs to be implemented to observe the evolution of its concentration both in the atmosphere as well as in aquatic sources. To support this objective, various $CH_4$ sensors, such as the solid state-based sensor [4-6], the calorimetric-based sensor [7, 8], and the photoacoustic-based sensor [9], have been developed. Although these sensors are relatively low-cost and can be used for long-term measurement, the majority of them are, however, also often sensitive to other gases. In addition, since most of these sensors require electrical power supply, they consequently cannot be easily deployed for *in situ* monitoring in marine environment.

Optical fiber sensors are one alternative solution which can be employed for long term *in situ* measurement involving no risk of explosion or short circuit since no on-probe electrical supply is required. Various optical fiber-based $CH_4$ sensors have been studied, such as the surface plasmon resonance (SPR) sensor [10,11], the waveguide Mach-Zehnder interferometer [12], and the evanescent wave multimode fiber (MMF) sensor [13]. These sensors exploit cryptophane-A supramolecules incorporated into an organic transparent polymer of polydimethylsiloxane (PDMS) or styrene acrylonitrile (SAN) which selectively trap and bind $CH_4$ molecules by a weak Van Der Waals force, as reported in [10-14]. This interaction leads to a proportional variation of the host polymer's bulk refractive index (RI) with the $CH_4$ concentration. In [10], it was shown that a linear response from a sensor exploiting cryptophane-A incorporated in PDMS, can be achieved with a sensitivity of $5.5\times10^{-6}$ RIU/nM $CH_4$.

SPR sensors operate principally on spectral modulation and typically require an optical spectrum analyzer (OSA), an optical time domain reflectometer (OTDR) or monochromators which are relatively costly and fragile. The Mach-Zehnder interferometer employs relative phase measurement, thus requiring relatively complex interrogation schemes and signal processing. The MMF evanescent wave sensor based on intensity modulation, on the other hand, while relatively simple and cost-effective to realize, has been reported to potentially offer very good resolution and sensitivity [13,15]. In our previous work [16,17], three operating RI regimes were identified and modeled in MMF-based refractometric sensor. This paper will thus describe development effort on intensity-based MMF sensor for methane gas detection through functionalized polymeric thin films encapsulating cryptophane-A supramolecular traps. In this work, SAN is employed as the host polymer, instead of PDMS to increase the sensitivity since the higher index of SAN could potentially shift the sensitive zone of sensor into the end of Zone II (i.e. the zone for which the sensing mechanism is influenced by evanescent wave absorption (EWA) and mode losses and which exhibits the highest sensitivity).

## II. SENSOR FABRICATION AND EXPERIMENTAL SET-UP

### A. Sensor fabrication

The MMF sensor can be realized by stripping a certain length of its cladding and buffer or coating. A polymer variant of SAN [12,14,16] with an RI value of 1.5496 RIU at a wavelength of 1052 nm, is used as the polymeric host. To synthesize the sensing film, a carefully-proportioned quantity of the 1,1,2,2,-tetrachloroethane solvent is used to dissolve both cryptophane-A and SAN, as reported in [17]. 10 mg of cryptophane-A in powder form is first dissolved in 2 ml of 1,1,2,2,-tetrachloroethane after which 100 mg of SAN powder are then added. To enable complete solution of SAN as well as ensure a homogenous distribution of the cryptophane-A supramolecules, the mixture is agitated for a minimum of 30 minutes. This solution is then deposited onto a 2 ± 0.1 cm length of bare MMF core and the thin film layer thus obtained is then smoothed with an optical fiber stripper with a predetermined hole size of 250 µm to obtain a homogenous sensing layer surface. The final coated MMF, an example of which is illustrated in Fig. 1, is then cured at 100 °C for 60 minutes.

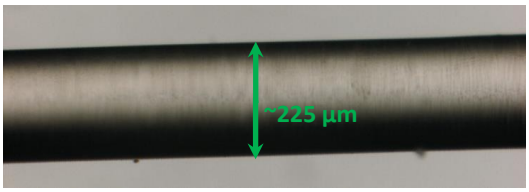


Fig. 1. Large scale image of sensitized MMF coated with SAN and cryptophane-A polymeric layer after curing.

As clearly shown in Fig. 1, the sensing layer is, at large scale, relatively homogenous and does not appear to contain any cryptophane-A residue or precipitates. This is subsequently employed for detecting $CH_4$ in parallel with an MMF reference arm which has been coated uniquely with SAN. Both fiber arms are then mounted in a differential configuration in order to compensate common mode noise (e.g. variation in ambient temperature, laser output power, vibration, etc).

### B. Experimental set-up

To set up the MMF refractometer for $CH_4$ measurement, the sensing region is held straight by a specially-designed support which also serves to reduce unwanted vibration or movement. The lead-in single-mode fibers (SMFs), being more resistant to bending and mechanical disturbances, are left free to be connected to the laser source, as illustrated in Fig. 2.

A 5L-volume air-tight flask wherein the MMF sensing and reference arms are deployed together, is used to contain the $CH_4$ gas during the experiment. Light from a single-mode laser with an operating wavelength of 1550 nm is coupled equally into the pair of lead-in SMFs fusion-spliced to the MMFs (see Fig. 2). The outputs from the sensing and reference MMFs are detected by a pair of identical photodetectors which are connected to a simultaneous 8-channel 16-bit National Instrument data acquisition system (DAQ).

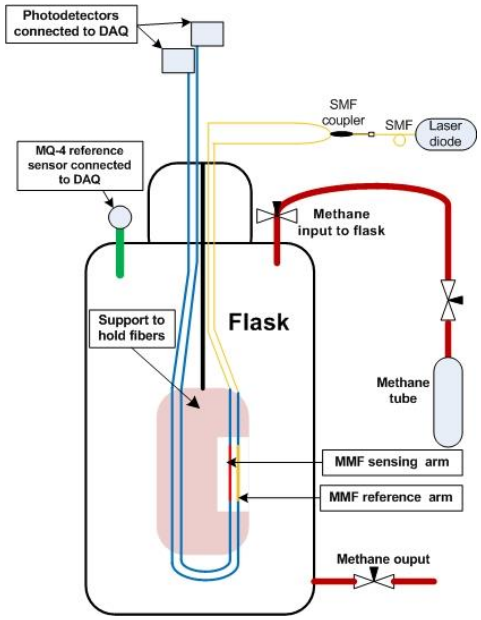


Fig. 2. Experimental set-up to measure atmospheric $CH_4$ concentration.

A small-diameter flexible tube is used to introduce $CH_4$ from the top of the flask, while another similar tube at the bottom of the flask enables to drain and reduce the $CH_4$ concentration in the flask. A commercial MQ-4 $CH_4$ sensor from Hanwei Electronics has also been employed as the reference $CH_4$ sensor with a dynamic range from 200 ppm to 10000 ppm for comparison.

## III. RESULTS AND DISCUSSION

To measure atmospheric $CH_4$ concentration in a controlled volume using the experimental set-up shown in Fig. 2, the output baseline signals from the sensing and reference MMFs as well as that from the MQ-4 sensor are initially recorded in the absence of $CH_4$. Methane is then progressively introduced into the container in a controlled manner. The inlet valve is closed when the output from reference MQ-4 sensor is at a maximum reading, corresponding to a controlled $CH_4$ concentration of 10000 ppm or 1% $CH_4$. This thus allows the entire sensor system to be calibrated. This level is maintained for approximately 60 seconds. In a second step, the $CH_4$ gas is drained by opening the small caps of the flask as well as the output valve to observe and record the response of the refractometric sensor during cyclic injection of $CH_4$. A sample of the measurement results for both increasing and decreasing $CH_4$ concentration is presented in Fig. 3.

The transmitted power of the MMF sensing fiber (blue line) decreases from an initial value of 3.78 V (i.e. without $CH_4$) to ~3.60 V, equivalent to 0.936 mW and 0.892 mW of transmitted optical power, respectively, and is detected by the photodetector set at a 10-dB gain level. These results represent a decrease of ~4.76 % of optical power for 10000 ppm of injected $CH_4$. The transmitted power subsequently returns to its original value when the flask is drained of $CH_4$. This transmitted power variation could be interpreted as the MMF sensor operating in the Zone II regime of MMF refractometer [17]. In this highly sensitive zone, optical power will decreases

with increasing index (i.e. increasing $CH_4$ concentration) and vice versa. Further, a difference in the measured signal levels between the sensing MMF (blue line) and the reference MMF (red line) is observed in Fig. 3. The sensing MMF which has been coated with a thin SAN film incorporating cryptophane-A is observed to transmit a higher power of ~3.78 V compared to ~2.84 V transmitted by the reference MMF. This difference could be attributed to the dissolved cryptophane-A which could potentially contribute to decreasing the bulk index of the host SAN polymer, and, hence, leading to an increase in the transmitted power.

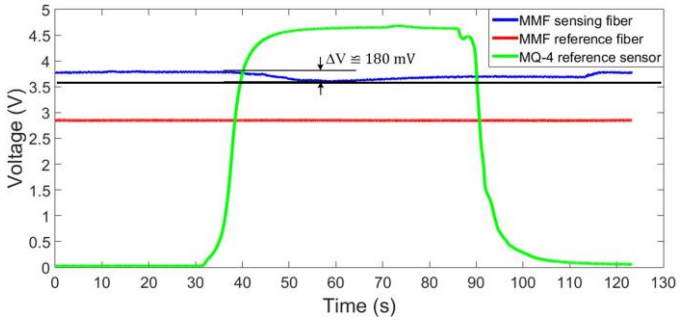


Fig. 3. Response of SMF-MMF refractometer and reference MQ-4 sensor to cyclic injection of 10000 ppm of methane.

Furthermore, while the sensing MMF responds to the presence of $CH_4$ as expected (blue line), the reference MMF (red line) remains stable throughout the experiments, thus exhibiting no sensitivity to $CH_4$. The optical power of the sensing MMF, measured in voltage by the photodetector, decreases when $CH_4$ is introduced. This clearly indicates an increase in the RI of the host polymer since the sensing MMF is in Zone II which exhibits a sharply decreasing power with increasing index [17]. More important, the response of the sensing MMF to cyclic variations in $CH_4$ concentration is relatively fast (~25 seconds) compared to [10] which reported a response time of ~1.8 minutes, thus making it highly suitable for applications where fast response is required, in particular to increase the temporal resolution of the measurements.

In terms of sensitivity, the MMF refractometer (sensing arm) is found to exhibit a relatively low response ($\Delta V$) of ~180 mV for 10000 ppm of $CH_4$ concentration. The reference MQ-4 sensor, on the other hand, is subject to a voltage variation of ~4.65 V. By assuming a linear variation of the polymeric SAN-Cryptophane-A index with $CH_4$ concentration [10], as well as a linear response approximation in Zone II [17], the sensitivity ($S$) of the fiber refractometer can then be predicted by

$$S = \left| \frac{\Delta V}{\Delta CH_4} \right| \tag{1}$$

where $\Delta V$ and $\Delta CH_4$ represent the response of the sensing MMF and the corresponding $CH_4$ concentration variation, respectively. According to (1), we thus obtain a sensitivity of 18µV/ppm (or 180 mV/10000 ppm). Corresponding to this sensitivity value, the limit of detection (LOD) can be estimated as a function of the noise level of the sensing MMF ($\sigma_{rms}$) by [16,17,19]

$$LOD = \frac{2.821}{S}\sigma_{rms} \tag{2}$$

The noise level achieved for the refractometer is currently ~1.187mVrms, corresponding to an LOD of 186 ppm or 0.0186% CH4 obtained by (2).

The LOD obtained is higher than another $CH_4$ sensor based on Mach-Zehnder interferometry (MZI) which has a reported LOD of 17 ppm [12], and is due to a relatively lower sensitivity of our MMF methane sensor. This lower sensitivity could potentially originate from a lower index variation of the cryptophane-A sensitized film in response to $CH_4$ variation. Nevertheless, our sensor is at least 100 times more sensitive than the evanescent wave absorption (EWA)-based fiber methane sensor using PDMS as the polymeric host, with a reported LOD of 2% [13]. It is also comparatively more sensitive than the 0.2% LOD (i.e. by more than 10 times) from the long-period fiber grating sensor reported in [14] which used SAN as the host polymer. While these results are promising, further work is needed to address issues of sensor repeatability and robustness. After an initial measurement cycle, subsequent repeated exposures of the sensors to $CH_4$ produce a reduced sensitivity performance. For every first measurement with this sensor, the $CH_4$ concentration can be detected with a relatively good response. However, the performance (i.e. sensitivity) decreases or is degraded for subsequent measurements or repeated utilizations. The origin of this repeatability problem is currently under investigation.

## IV. Conclusions

A polymer variant based on SAN (or styrene acrylonitrile) is employed in the MMF refractometer for $CH_4$ detection. Here, 1,1,2,2,-tetrachloroethane has been used as the solvent to completely dissolve the cryptophane-A supramolecules. The use of SAN as the polymeric host enables a relatively uniform sensitized layer to be deposited on the fiber surface. The experimental results demonstrated a relatively fast response (~25 seconds) achieved by the functionalized MMF refractometer and a detection limit of ~186 ppm or 0.0186 % $CH_4$ has been obtained. While improvement is needed to match reported MZI sensors performance [12], this result is better than both the EWA-based $CH_4$ fiber sensor and the long-period grating sensor which had detection limits of 2 % [13] and 0.2 % [14], respectively. Future work will look to improve sensitivity further and address the issue of sensor repeatability in order to meet the needs demanded by real world applications.

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## REFERENCES


[1] J.T. Houghton, G.J. Jenkins, and J.J. Ephraums, “Climate Change,” The IPCC assessment, Cambridge University Press: 1990.

[2] https://climatechangeconnection.org/emissions/co2-equivalents.

[3] https://www.epa.gov/ghgemissions/overview-greenhouse-gases.

[4] J. P.Kennett, K. G. Cannariato, I. L. Hendy, and R. J. Behl*, "*Methane Hydrates in Quaternary Climate Change: The Clathrate Gun Hypothesis*," Spec. Publ. Ser.*, vol. *54*, Washington, *D. C.*: 2003.

[5] L. de Angelis and R. Riva, “Selectivity and stability of a tin dioxide sensor for methane,” *Sens. Actuators B*, vol. 28, pp. 25-29, 1995.

[6] F. Quaranta, R. Rella, P. Siciliano, S. Capone, M. Epifani, L. Vasanelli, A. Licciulli, and A. Zocco, “A novel gas sensor based on $SnO_2$/Os thin film for the detection of methane at low temperature,” *Sens. Actuators B*, vol. 58, pp. 350-355, 1999.

[7] B. W. Licznerski, K. Nitsch, H. Teterycz, P. M. Szecowka, and K. Wisniewski, “Humidity insensitive thick film methane sensor based on $SnO_2$/Pt,” *Sens. Actuators B*, vol. 57, pp. 192-196, 1999.

[8] P. N. Bartlett and S. Guerin, “A micromachined calorimetric Gas Sensor: an application of electrodeposited nanostructured palladium for the detection of combustible gases,” *Anal. Chem.*, vol. 75, pp. 126-132, 2003.

[9] H. Debeda, L. Dulau, P. Dondon, F. Menil, C. Lucat and P. Massok, “Development of a reliable methane detector,” *Sens. Actuators B*, vol. 44, pp. 248-256, 1997.

[10] C. Boulart, M. C.Mowlem, D. P. Connelly, J.-P. Dutasta, and C. R.German, “A novel, low-cost, high performance dissolved methane sensor for aqueous environments,” *Opt. Express*, vol. 16, pp. 12607–12617, 2008.

[11] C. Boulart, R. Prien, V. Chavagnac, and J-P. Dutasta, “Sensing dissolved methane in aquatic environments : an experiment in the central Baltic Sea using surface plasmon resonance,” *Environmental science & technology*, vol. 45, pp. 8582-8590, 2013.

[12] F. T. Dullo, S. Lindecrantz, J. Jágerská, J. H. Hansen, M. Engqvist, S. A.Solbø, and O. G.Hellesø, "Sensitive on-chip methane detection with a cryptophane-A cladded Mach-Zehnder interferometer," *Opt. Express*, vol. 23, pp. 31564-31573, 2015.

[13] M. Benounis, N. Jaffrezic-Renault, J.-P. Dutastab, K. Cherif, and A. Abdelghani, “Study of evanescent wave optical fibre sensor for methane detection based on cryptophane molecules,” *Sens. Actuators B*, vol. 107, pp. 32–39, 2005.

[14] J. Yang, Ch. Tao, X. Li, G. Zhu, and W. Chen, “Long-period fiber grating sensor with a styrene-acrylonitrile nano-film incorporating cryptophane A for methane detection,” *Opt. Express*, vol. 19, pp. 14696–14706, 2011.

[15] J. Yang, L. Xu and X. Cheng, “An optical fiber methane gas sensing film sensor based on core mismatch,” *Chin. Opt. Lett.*, vol. 8, pp. 482-484, 2010.

[16] H. Apriyanto, G. Ravet, O. Bernal, M. Cattoen, F. Lizion, H. C. Seat, and V. Chavagnac, “A multimode fiber refractive index sensor,” in *Proc. IEEE Sensors*, 2016.

[17] H. Apriyanto, G. Ravet, O. Bernal, M. Cattoen, F. Lizion, H. C. Seat, V. Chavagnac, F. Surre, and J. H. Sharp, “Comprehensive modeling of multimode fiber sensors for refractive index measurement and experimental validation,” *Sci. Rep.*, vol. 8, pp. 1-13, 2018.

[18] J. Yang, J. Huang, X. Li, S. Li, B. Luo, C. Tao and W. Chen, “High-sensitivity long-period fiber grating sensor with SAN/cryptophane A for coal mine gas detection,” *Chin. Opt. Lett.*, vol. 11, pp. *080601,* 2013.

[19] S. M. Lindecrantz, “Waveguide Mach-Zehnder interferometer for measurement of methane dissolved in water,” PhD dissertation, The Arctic University of Norway, 2016.

[20] J. W. Steed and J. L. Atwood, “Supramolecular chemistry,” John Wiley & Sons, 2013.