ULTRA-LOW NOISE FIBRE OPTIC SENSOR FOR LOW LIMIT OF DETECTION IN AQUEOUS MEDIUM

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ABSTRACT
Water from some sources contains waterborne pollutants like lead or cadmium cations, which are toxic to both human beings and animals even at low concentrations. This calls for sensitive, low cost and portable instruments like 'optrodes' (optical sensors) that can be applied for on-site detection of these pollutants. However, the limit of detection of existing optical sensors is still higher than the recommended safety standards, due to the detector noise superimposed to the low level signals arising from lower dissolved pollutant concentrations. To solve this problem, we introduced a self-referenced evanescent wave optical fibre as a transducer, and a 'light balance' with lock-in read-out for minimum noise levels. From these techniques, we report low noise levels of 64 nV due to lock-in detection and a lower LoD as compared to earlier transducers. This was demonstrated with a clear signal response of ~10 μV from very low levels of dissolved Zn^{2+} (50 nM). With suitable sensitizer, our transducer has a potential application to field measurements of low concentrations of waterborne pollutants.
Keywords: Evanescent wave sensor, Lock-in detection, Dual beam detection, 1-(2-pyridylazo)-2-naphthol

INTRODUCTION

Access to clean and safe drinking water (Iqbal *et al*., 2011) by both plants and animals is a primary objective of every Nation. Therefore, the levels of waterborne pollutants in water sources are important in guiding various countries to follow the set safety standards (Organization, 2011) in provision of water to her people and managing aquatic animals. Heavy metals are one class of such waterbone pollutants and some of these pollutants, Cd^{2+} (Gunnlaugsson *et al.*, 2004) and Hg^{2+} (Zhou *et al.*, 2014) are toxic even at low quantities. This demonstrate clearly the need for on-site portable techniques that can continuously monitor the levels of pollutants and relay quantitative information to a central office for appropriate actions to be taken before a disaster occurs. However, the output signal from existing spectrophotometers and hand-held portable instruments for detecting waterborne pollutants is associated with Johnson noise from resistors within their internal circuitry and shot noise due to their photodetectors (Pauchard *et al.*, 2000). These instruments detect the presence of waterborne pollutants by transducing the optical signal carrying the pollutant quantitative information into an electrical signal.

Therefore, with very low concentrations of pollutants in the sample, the output signal is in a pool of noise and raises the limit of detection (LoD). In order to push the LoD lower, researchers have developed a number of sensitive techniques based on atomic absorption spectroscopy (Chiu *et al.*, 2003), atomic emission spectroscopy (Xiong *et al.*, 2006) and mass spectroscopy (Wang *et al.*, 2001) to detect these waterborne pollutants. These techniques require expensive instrumentation (Liu *et al.*, 2012) and prior separation and pre-concentration procedures (Citak *et.al.* 2009) before analysis of samples. Due to these shortcomings, a number of cheaper and on site real time analytical techniques for heavy metals dissolved in water have been reported; for instance, for detection of dissolved Cu^{2+} in water with reported LoD 0.36 μM (Li *et al.*, 2015) and for detection of Hg^{2+} with reported LoD 0.5 μM (Li *et.al.*, 2014). However, LoD in these techniques are still higher than the set safety standards (Organization, 2011) and need to be pushed down further.

As a solution to these shortcomings, we have demonstrated earlier (Tuwei *et al*., 2016) implementing lock-in detection and lowered the LoD 28 times better than (Albero *et al*., 2002) under the same experimental conditions by improving signal to noise ratio. In this paper, we illustrated experimentally, how we minimized both detector and source of light (LED, laser diode) drift by introducing self-referencing technique. We also show how the low noise signal from Lock-in detection translates into a lower LoD. Lock-in detection is achieved by using a digital lock-in amplifier, which is configured (Medina-Rodriguez *et al*., 2014) to select the required signal at a specific frequency of interest by the user from a spectrum of noise and more so for low level signals due to very low concentration of dissolved water pollutants. Self-referencing was accomplished by a light balance circuits (Hamamtsu, 2008) for low drift applications.

MATERIALS AND METHODS

A simplified block diagram for our designed low noise evanescent wave sensor based on fibre optic and lock-in detection is shown in Figure 1. A detailed designed procedure and instrumentation is documented in (Tuwei et al., 2016. For single detector mode, we removed photodetector PD_1, reference beam and subtractor circuit (R–S) and only work with a single photodetector (PD_2) in the sample beam. There was no point of using the neutral density filter, ND in this mode.

For drift and noise analysis, we modulated the LED (L-7113QBC-D, Kingbright) with an AC signal of amplitude 3.6 V r.m.s from lock-in amplifier REF output and recorded the Lock-in output voltage (DC signal) using LabVIEW routine. We then reduced the amplitude to 1.2 V and recorded the Lock-in output voltage. Instead of using the dual detector (Tuwei et al., 2016), we used a single photodiode (OSD5-5T, Centronic) in the sample beam without reference beam. The signal from sample beam was connected to i/v converter and fed the resulting voltage into the lock-in amplifier for processing and recording the Lock-in voltage output voltage.

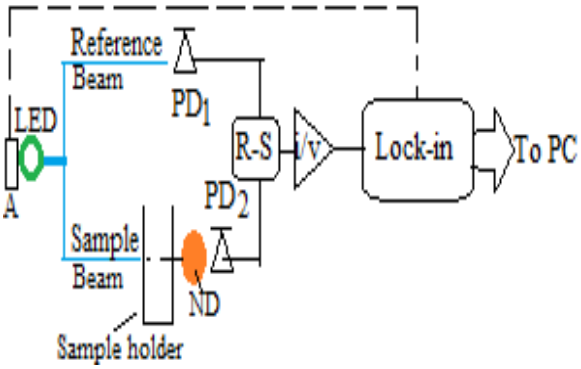


Figure 1. Schematic of dual beam evanescent wave sensor based on fibre optic for waterborne pollutant detection. A–Adder circuit, ND–Neutral density filter, PD1 and PD2 are photodetectors while PC–personal computer. R–S is the subractor circuit where R is reference beam while S is the sample beam.

Finally, we fabricated a 20 cm long fibre where a 2 cm section was stripped in the middle and coated with 1-(2-pyridylazo)-2-naphthol (PAN) as described earlier (Tuwei et al., 2016). Then run though the sample holder and light of λ = 555 nm from a modulated LED (SSL-LX5093PGD, Lumex) was propagated through the fibre to probe the resulting complex between Zn^{2+} and PAN. A modulation of with 1.2 V and frequency of 5.641 kHz was used.

RESULTS AND DISCUSSION

Single Verses Double Beam Detection

For a single detector, the signal drifted from 0.36 mV to 0.93 mV in 25 minutes, then stabilized as shown in figure 2 (blue curve). It implies therefore that the instrument should be run for 25 minutes before introducing a sample for measurement. This is attributed to the rise in junction temperature of the LED (Wang *et al.*, 2015,) which is fabricated from InGaN semiconductor. The increase in temperature increases the forward dc current (Xi *et al.*, 2005), hence increases charge carriers with time until it reaches the equilibrium concentration and levels off. It has noise levels of 0.0669 mV and this will raise the LoD. For dual detection with the same LED and 50/50 beam splitter, there is essentially no drift as can be seen clearly in figure 2 for 1.2 V modulation and noise levels of 0.0014 mV, which is ~ 48 times lower than in single detector. However, there was a slight drift for 3.6 V modulation compared to the 1.2 V modulation signals in dual detection. Therefore from this observation, dual detection with 1.2 V is adopted for sensing low concentrations of waterborne pollutants in our sensor.

Modulation Amplitude

To account for the different results in 1.2 V and 3.6 V modulation (mod in the figure legend) in dual detection, we used the concept of shot noise in a semiconductor. The number of photons reaching the two detectors per second is depends on the modulation amplitude of the ac signal for a constant LED bias voltage, Vdc. Therefore, for 3.6 V modulation amplitude, there are more photons reaching the detectors per second than in 1.2 V modulation. Consequently, the shot noise (Pauchard *et al.*, 2000) in 3.6 V modulation is higher than in 1.2 V modulation and causes more fluctuations as indicated in figure 3. The slight drift is suspected to be associated with PD_1 receiving increasing photons per second continuously compared to PD_2.

Waterborne Pollutants System Noise and Sensing

Figure 4 (a) shows the dynamic response for a 50 nM and 100 nM aliquots of Zn^{2+} solutions. We used Zn^{2+} as a representative of waterborne pollutants in aqueous media and that it binds to the chosen sensitizer (PAN). The blank signal (part of the response between 0 and 60 seconds before introducing the 50 nM Zn^{2+}) is expanded as indicated in figure 4 (b) (Note the units on y-axis). The noise levels is 64 nV calculated as standard deviation of the blank signal. The signal response for the dissolved 50 nM Zn^{2+} is ~10 µV which is above the noise levels.

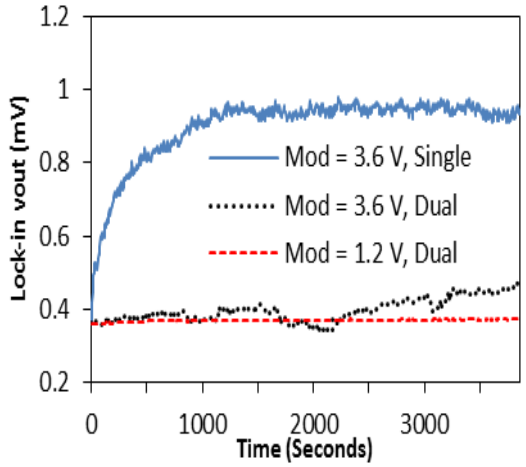


Figure 2. Comparison of the signal drift in single and dual detector comfiguration in evanescence wave sensor

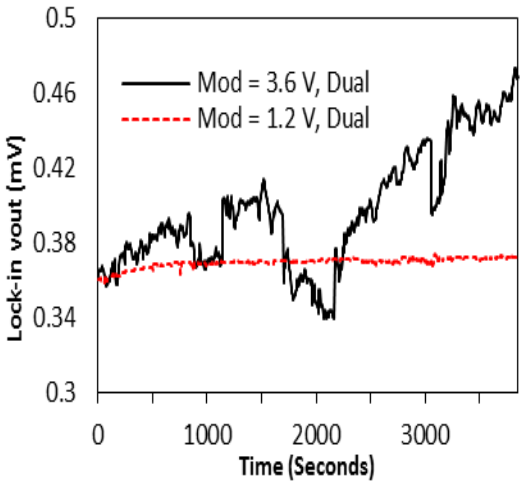
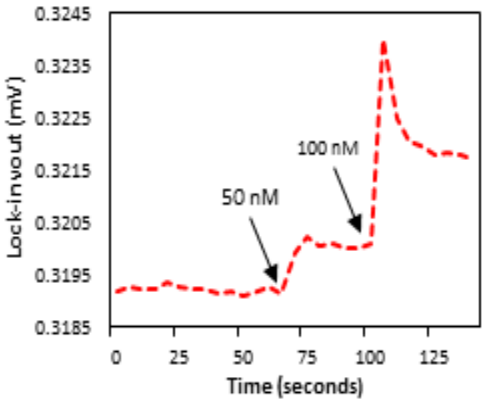
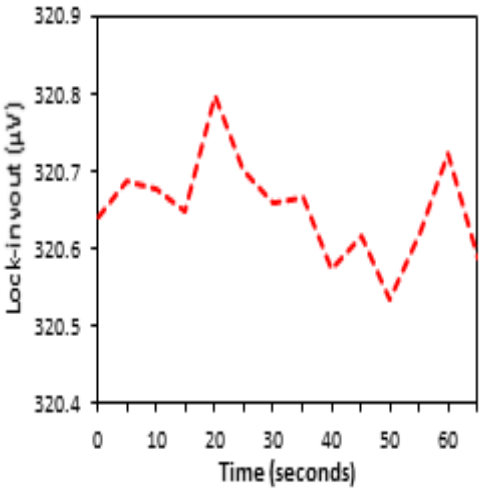


Figure 3. Effects of modulation amplitude on output signal from evanescence wave sensor.



(a)



(b)

Figure 4. Signal response of the sensitized fibre to 50 nM and 100 nM Zn^{2+} under (a) HEPES buffer and (b) Blank signal.

The increase in signal shown in figure 4 (a) when 50 nM and 100 nM Zn^{2+} solutions were titrated into the sample holder is due to the interaction of PAN with Zn^{2+} (Cheng *et al*., 1955, Safari *et al*., 2011). One Zn^{2+} is bound to the two PAN molecules and formed a complex with 555 nm absorption peak (Gupta *et al*., 2015) which matches the chosen wavelength of proping light in the fibre optic. Therefore the evanescent wave (Kumar *et al*., 2002) from the fibre optic is absorbed by the PAN + Zn^{2+} complex and lead to intensity loss in the proping light. This absorbed light (intensity loss) by PAN + Zn^{2+} complex in the sample beam is detected by the instrument as shown by a rise in the signal observed.

CONCLUSION

Dual detection is better than using a single detector in sensor designed to detect low concentrations of waterborne pollutants due to the low drift. By introducing a self- referenced evanescent wave optical fibre as transducer, and a 'light balance' with Lock-in read-out for minimum noise levels, we demonstrate a clear signal response of ~ 10 µV from our instrument to very low levels (50 nM Zn^{2+}) of dissolved waterborne pollutants. We have also demonstrated noise level of a blank signal as lower as 64 nV due to lock-in detection, which translates to lower LoD from our approach.

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