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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 (e.g lead or cadmium cations) toxic to both human beings and animals even at low concentrations. This calls for sensitive, low cost and portable instruments that can be applied for on-site detection of these pollutants, e.g. ‘optrodes’ (optical sensors). The limit of detection of existing optical sensors is still higher than the recommended safety standards, which is attributed to the detector noise superimposed to the low level signal. In our quest 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. We coated a thin film of 1-(2-pyridylazo)-2-naphthol as a Zn²⁺ sensitizer on a 2 cm stripped section of a 20 cm long sensing fibre optic and run through a sample vessel. 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 to very low levels (50 nM) of dissolved Zn²⁺. 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, Noise level, 1-(2-pyridylazo)-2-naphthol*

INTRODUCTION

The levels of waterborne pollutant are important in guiding various countries to follow the set safety standards (Organization, 2011) in provision of water to people and managing aquatic animals. This is because some of the water pollutants, Cd²⁺ (Gunnlaugsson et al., 2004) and Hg²⁺ (Zhou et al., 2014) are toxic even at low quantities. Recently in Lake Naivasha, which is an important source of fish to people living in Lake Naivasha basin (Otachi et al., 2014), a shoal of fish deaths were reported and suspected to have been caused by oxygen depletion (Njiru et al., 2015) due to algae bloom. 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 raise 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 $0.36 \mu\text{M}$ (Li et al., 2015) and for detection of Hg^{2+} with reported LoD $0.5 \mu\text{M}$ (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 an evanescent wave fibre optic sensor (Tuwei et al., 2016) based on lock-in detection to lower the LoD by improving signal to noise ratio. In this work, we illustrated experimentally, how we have 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 translate 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 Fig. 1. A detailed designed procedure and instrumentation is documented in (Tuwei et al., 2016). Basically, it consists of modulated source of light ie LED, beam splitter (BIF400-VIS-NIR, Ocean Optics) and two photodetectors PD_1 and PD_2 (OSD5-5T, Centronic) connected such that their output currents are subtracted electrically as indicated by $R - S$ ie as “light balance circuit” (Hamamtsu, 2008). Here, R and S are signals from reference and sample beams respectively. The differential current Δi , which carries the quantitative information for water pollutant, is conditioned by current to voltage converter (i/v) (OPA380, Texas Instruments) and fed into the lock-in amplifier (USBLockIn250, Anfatec) for processing and displayed to the user on a personal computer (PC). To zero-in the instrument for 0 V output signal, we incorporated a grey wheel density filter (54079, Edmund optics) into the sample beam to attenuate light when the two photodiodes are perfectly aligned to receive equal light intensities.

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 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 vout DC signal using LabVIEW routine. We then reduced the amplitude to 1.2 V and also recorded the Lock-in vout. Instead of using the dual detector in our instrument (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 recorded the Lock-in vout.

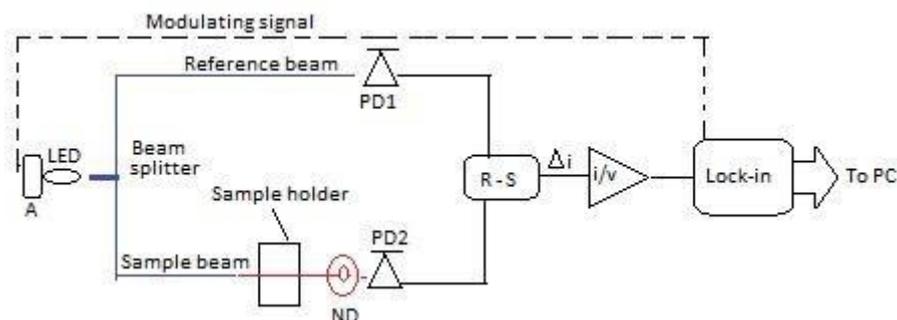


Figure 1. Schematic of dual beam evanescent wave sensor based on fibre optic for waterborne pollutant detection. A–Adder circuit, ND–Neutral density filter, PD1 and PD2 are photodetectors while PC–personal computer. R–S is the subtractor circuit where R is reference beam while S is the sample beam.

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 through the sample holder and light of $\lambda = 555$ nm from a modulated LED (SSL-LX5093PGD, Lumex) was propagated through the fibre to probe the resulting complex between Zn^{2+} and PAN. We used a modulation of with 1.2 V and frequency of 5.641 kHz.

RESULTS AND DISCUSSION

Single versus Double Beam Detection

For a single detector, the signal drifted from 0.36 mV to 0.93 mV in 25 minutes, then stabilize as shown figure 2 (blue curve). This mean the instrument should be run for 25 minutes before introducing a sample for measurement. This is attributed to the temperature rise of the LED which is fabricated from InGaN semiconductor. The increase in temperature increases the 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 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 in dual detection, we used the concept of shot noise in a semiconductor. The number of photons reaching the two detectors per second is depend on the modulation amplitude of the ac signal for a constant LED bias voltage, V_{dc} . 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 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 PD₁ receiving increasing photons per second continuously compared to PD₂.

System Noise and Sensing of Waterborne Pollutants

To demonstrate how low noise in dual detection translate into lower LoD, we coated a thin film of 1-(2-pyridylazo)-2-naphthol on a 2 cm stripped section of a 20 cm long sensing fibre optic as a Zn^{2+} sensitizer and run through a sample vessel. Then titrated aliquots of Zn^{2+} solutions into sample vessel as described earlier (Tuwei et al., 2016). Figure 4 (a) shows the dynamic response for a 50 nM and 100 nM aliquots of Zn^{2+} solutions. The blank signal (part of the response between time 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 in the blank signal is 64 nV and the signal response for the dissolved 50 nM Zn^{2+} is ~ 10 μV which is well above the noise levels.

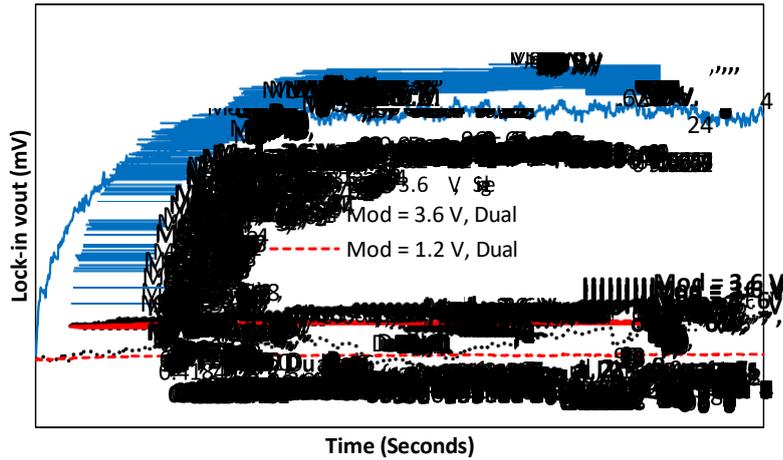


Figure 2. Designed evanescence wave sensor all the symbols in this schematic

The rise in signal in figure 4 (a) when 50 nM and 100 nM Zn^{2+} solution was titrated into the sample holder is due to interaction of PAN with Zn^{2+} as detected by the instrument. In this case PAN and Zn^{2+} formed a complex with peak absorption λ that matched the λ of propagating light in the fibre optic. Therefore the evanescent wave along the surface of the fibre optic is absorbed by the PAN + Zn^{2+} complex. The absorbed light in the sample beam is shown by a rise in the signal as observed.

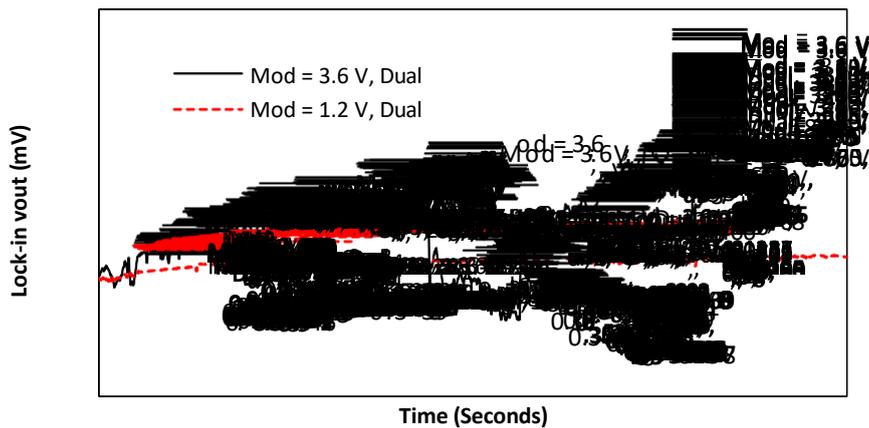


Figure 3. Designed evanescence wave sensor all the symbols in this schematic

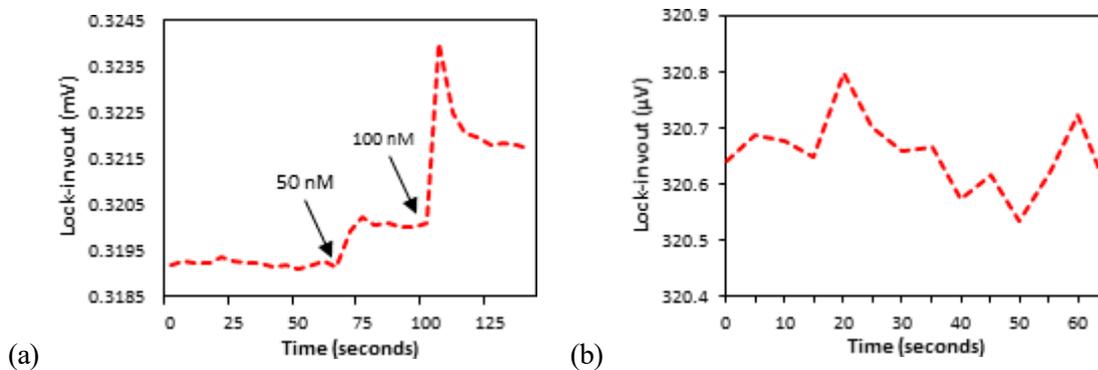


Figure 4. Signal response of the sensitized fibre to 50 nM and 100 nM Zn^{2+} under (a) HEPES buffer and (b) Blank signal

CONCLUSION

Dual detection is better than using a single detector in sensors designed to detect low concentrations of waterborne pollutants due to 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 $\sim 10 \mu\text{V}$ from our instrument to very low levels (50 nM) of dissolved zinc cations. We have also demonstrated noise level of a blank is 64 nV due to lock-in detection when measured within 60 seconds and 1.4 μV noise levels when a signal is measured for approximately 1 hour, which translates to lower LoD from our approach.

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