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Fibre optic absorbance meter with low limit of detection for waterborne cations

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Abstract

We report an evanescent wave based fibre optic absorbance meter that enables the colorimetric detection of waterborne cations with water insoluble chromoionophoric sensitisers. This establishes an alternative to the PVC membrane based transducers that are conventionally used for this purpose. Here, a water insoluble sensitiser is coated as a thin film on an unclad section of a multimode optical fibre to overlap with the evanescent field of a light beam propagating along the fibre core. The colorimetric response of the sensitiser when in contact with waterborne cation leads to increased absorption of virtual photons associated with the evanescent field. The resulting intensity loss of the propagating beam is detected by a bespoke newly designed self- referenced evanescent wave absorbance meter with beam intensity modulation and Lock-in amplification. We validate our transducer with the well characterised water insoluble sensitizer, 1-(2-pyridylazo)-2-naphthol (PAN), for the detection of aqueous Zn^{2+} cations. We find a limit of detection (LoD) of 54 nM Zn^{2+}, 28 times lower compared to a PVC membrane based sensor using same sensitiser for same cation (Albero et al., Journal of Pharmaceutical and Biomedical Analysis 29 (2002), 779). Our evanescent wave absorbance meter can easily be adapted to other colorimetric sensitisers, including chromoionophoric complex forming macrocycles.

Keywords: Limit of detection, Fibre optic sensor, evanescent wave, cation, Lock-in amplifier, PVC membrane.

1. Introduction

Pollution caused by waterborne cations in natural waters is a great concern to the world health organisation [1] due to the fact that some waterborne cations, e.g. Hg^{2+} [2] and Cd^{2+} [3] are toxic to animals and human beings even at nanomolar levels. Consequently, a number of sensitive techniques, e.g. atomic absorption spectroscopy [4], atomic emission spectroscopy [5, 6] and mass spectroscopy [7] have been developed to detect cations at low concentrations. However, these techniques require expensive instrumentation and laboratory infrastructure that is not easily portable to the point of need [8].

Colorimetric chemical sensors, known as ’optrodes’, promise a lower cost, portable alternative [9, 10]. In pursuit of viable optrodes, organic chemistry has delivered a variety of coloured molecules that can chelate metal cations with a consequential change in their optical absorption bands. These are known as ‘chromoionophores’, and a classical example is 1-(2-pyridylazo)-2-naphthol (PAN) [11], which forms 2:1 chelate complexes [PAN-M^{2+}-PAN] with a number of bivalent metal cations. More recently a range of chromoionophoric macrocycles (calixarenes [12, 13], porphyrines [14], phthalocyanines [15, 16]), and conjugated polymers bearing crown ether ligands [17], have been reported with sometimes highly selective chelating of metal cations in their central cavity. However, PAN and many macrocycles are often almost insoluble in water [18, 19], divorcing them from immediate application in an aqueous medium, a severe limitation for biology or the natural environment where water is the primary solvent. For characterisation, chromoionophoric macrocycles may be dissolved and tested in polar aprotic solvents like acetonitrile, dichloromethane [20] or dimethyl sulfoxide [21] which co- dissolve some metal salts (e.g. picrates). For applications involving an aqueous medium, the contact between insoluble chromoionophore and waterborne cations is conventionally mediated by embedding the chromoionophore in plasticised PVC membranes [22, 23]; a theoretical treatment is in [24]; or in sol- gel matrices [25].

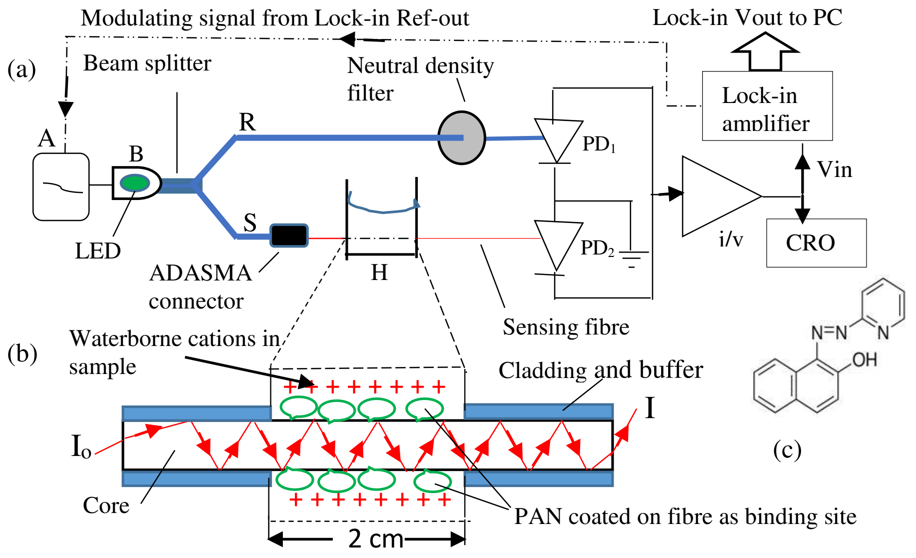
Here we demonstrate an alternative to PVC membranes for colorimetric detection of waterborne cations with chromoionophoric sensitisers that are insoluble in water. While PVC membranes or sol- gel matrices enhance the contact between aqueous medium and insoluble sensitiser, we enhance the contact between insoluble sensitiser and the light that probes its absorbance instead. We apply a thin chromoionophore film as a sensitiser onto the unclad core of an optical fibre that carries a light beam while immersed in an aqueous sample. At the fibre core / sensitiser interface, an evanescent wave leaks into the sensitiser coating for a fraction of a wavelength, but cannot permanently escape. However, when the chromoionophore binds waterborne cations across the nearby sensitiser / water interface, the evanescent wave overlaps with the resulting absorption band, leading to reduced intensity in the propagating beam. A few similar evanescent wave fibre optic sensors for dilute analytes have been reported recently, *e.g.* for dyes in wastewater [26], humidity [27], and mercury vapour [28], but not for the detection of waterborne cations with organic chromoionophores. The emphasis of our work is on the development of a bespoke fibre optic absorbance meter which allows the detection of weak evanescent wave absorbance. We combine commercially available electronic and fibre optic parts into a self- referenced 'light balance' absorbance meter with probe beam modulation for Lock- In amplification that represents a new benchmark for evanescent wave fibre optrodes.

We test our instrument on the chromoionophore PAN (82960, Sigma Aldrich) to detect waterborne Zinc (Zn^{2+}) cations, and demonstrate a significantly lower limit of detection (LoD) compared to Zn^{2+} detection using PAN embedded in a PVC membrane [29].

2. Experimental

2.1. Dual beam evanescent wave absorbance meter

Our dual beam evanescent wave sensor consists of an electrical and a fibre optic part. These are interlinked at two points, namely a light emitting diode (LED) that converts an electrical drive signal into light that is fed into the fibre optic system, and a pair of photodiodes PD1 and PD2 (OSD5-5T, Centronic) that converts light back into an electrical signal after passage through the fibre optic part. The electrical part itself is divided into a drive and a measurement section, which are both coupled to a digital Lock-in amplifier (USB LockIn250, Anfatec). In the drive section, the modulation output of the Lock-in amplifier delivers an ac voltage (amplitude = 3.6 V (peak), f = 5.641 kHz) to an ac/dc adder circuit which adds 8.15 V dc bias to the ac signal. This ac + dc voltage drives an LED (SSL-LX5093PGD, 555 nm) via a serial resistor (R_{LED} = 180 Ω) that couples into the fibre optic part (see Fig. 1). In the fibre optic system the beam is split by a fibre optic beam splitter (BIF400-VIS-NIR, Ocean Optics) into a sample and a reference beam, both of which are eventually projected onto one of the pair of PDs which belong to the measurement section of the electrical part. The PDs are connected so that their photocurrents are subtracted and then converted into a voltage by a transimpedance amplifier (OPA380, Texas Instruments) with feedback resistor, $R_f = 100\ k\Omega$. This differential setup is known as a 'light balance' [30], albeit the light balance is not usually modulated. The ac voltage output of the transimpedance amplifier (V_{in}) is fed into the Lock-in amplifier signal input, which delivers a dc output voltage V_{out} that is proportional to the difference of ac light intensities at the two PDs, and hence proportional to absorbance A in the sample beam as long as $A << 1$. V_{out} is recorded *vs.* time with a LabVIEW routine. The use of modulation and Lock-in detection enables measurement of V_{out} with very low noise [31, 32] and in the presence of ambient light. Note that the detection of light intensity ratio, as in a conventional dual beam spectrometer, rather than intensity difference as we do here, would cancel intensity modulation and thus disable Lock-in detection. The fibre optical part uses PM20-SMA and S05LEDM connectors (Thorlabs) to couple the modulated LED light into a fibre optic beam splitter to split the signal into sample- and reference beam. The sample beam is coupled via ADASMA mating sleeves (Thorlabs) into a sensitised optical fibre that runs through a sample vessel via sealed feedthroughs, in our case a buffered solution of waterborne cations. The sample beam is eventually projected onto one photodiode of our PD pair. The reference beam is projected onto the other PD across an adjustable mounted neutral density filter wheel (54079, Edmund optics). Fig. 1 shows a schematic of our dual beam evanescent wave sensor. Fig. 1d is a screenshot of V_{in}, *i.e.* the signal delivered by the light balance after I/V conversion. The information on evanescent wave absorbance is in the modulation amplitude (not the phase) of V_{in}. Note the noisy character of V_{in} which is then 'cleaned up' into a low noise dc V_{out} signal by the Lock- In amplifier, as we will show later (Fig.s 2, 3, 5).



(d)

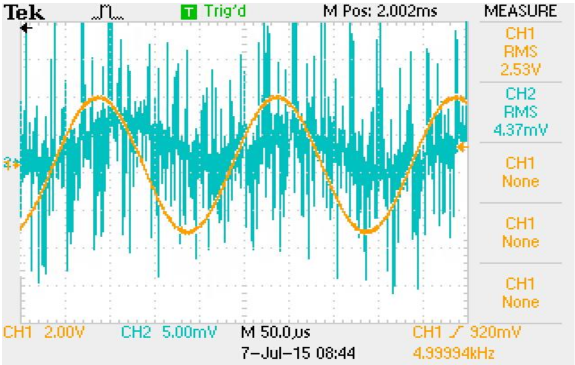


Fig. 1. **(a)** Schematic diagram of our dual beam evanescent wave sensor design: A is the ac/dc adder circuit, B is a PM20-SMA/S05LEDM connector, R is the reference beam, S is the sample beam, H is the sample vessel, and i/v is the transimpedance amplifier. **(b)** illustrates the stripped and PAN- coated section of the fibre. I_o and I are light intensities in and out of the fibre respectively. **(c)** Chemical structure of PAN sensitiser. **d:** Oscilloscope screenshot of V_{in}, *i.e.* the signal of the light balance after I/V conversion, but before Lock- In processing (blue, 5 mV / division). For comparison, the reference signal that was used for LED modulation is also shown (orange, 2V / division).

The absorbance meter was calibrated by inserting cuvettes with samples of known absorbance A into the sample beam path which yielded an instrumental sensitivity of $\Delta V_{out} / \Delta A = 13700$ mV.

2.2. Preparation of sensing fibres

As the ion sensitive element of our dual beam evanescent wave sensor, we used a length of 20 cm multimode optical fibre (FT400UMT, Thorlabs), with silica core of diameter 400 µm and a 25 µm polymer cladding that we cut from a fibre reel. The fibre was cleaved with S90R cleaver (Thorlabs) at 90 degrees to the fibre length and polished with lapping papers (Thorlabs) starting with LFG5P with 5 µm grit, LFG1P with 1 µm grit, and finally LFG03P with 0.3 µm grit to enhance the coupling of light into the sensing fibre. In the middle of this fibre, we stripped a section of 2 cm fluoropolymer (tefzel) buffer mechanically using a scalpel to expose the cladding polymer. We then wet a small section of kimwipes with acetone to wipe off the cladding to expose the fibre's silica core for a length of 2 cm. This was washed with deionized (DI) water, blown dry under a nitrogen flow and fully dried at 90 ^{o}C for 1 hour before coating. We then sprayed bidentate chelating agent PAN from 1 mM solution in chloroform (for comparison also from 10 mM solution) onto the stripped section of the fibre using a hand pumped 5 ml spray bottle. The chromoionophoric response of PAN to a range of bivalent and trivalent cations (e.g. Zn^{2+}, Cu^{2+}, and Al^{3+}) is well established [33]. In particular, when PAN chelates waterborne Zn^{2+}, its optical absorption at 555 nm increases, hence our choice of a 555 nm LED. Sensitised fibres were dried under vacuum and then immersed into HEPES buffer solution (10 mM HEPES acid, H3375 and 20 mM HEPES sodium salt, H7006, both from Sigma Aldrich) for 12 hours in a fridge below 4 ^{o}C as preconditioning prior to use. Fibres were cooled during incubation to avoid HEPES degradation. The same concentration of HEPES buffer solution was used throughout the experiment.

2.3. Experimental protocol

A sensitised fibre is run through a sampling vessel filled with 8 mL HEPES buffer solution via sealed feedthroughs so that the sensitised central section is submerged in buffer, and light from the LED is split using beam splitter and driven through both sample and reference paths. Initially, the neutral density filter wheel is trimmed so that sample and reference intensity become near equal, i.e. Lock- In V_{out} is near zero. We did not trim to exact zero to avoid phase noise. We first added a large amount of concentrated $ZnNO_3$ stock solution into the sampling vessel to reach a concentration of 2mM Zn^{2+} (excess) to find the maximum possible V_{out} response, and to determine how long the fibre needs to equilibrate after analyte is added. Using another sensitized fibre and the same HEPES buffer, we then repeatedly added small amounts Zn^{2+} from a 0.1 mM $ZnNO_3$ stock solution using a microlitre syringe to raise concentration from zero in steps of 50 nM (initially) or 100 nM. After addition of each Zn^{2+} droplet, we recorded the consequential change in V_{out} *vs.* time for 30 seconds (50 nM steps) / 60 seconds (100 nM steps) before adding more analyte. We tested a number of fibres to confirm they gave practically identical responses. To establish selectivity we carried out control experiment adding mono- and divalent alkaline / earth alkaline cations via their chlorides. Recovery was studied by adding an excess of cation sequestration agent EDTA. EDTA and chlorides were sourced from Aldrich.

3. Results and Discussion

Fig. 2 shows the Lock-in output voltage V_{out} for a sensitised fibre recorded *vs.* time when a large amount of $ZnNO_3$ is added to 8 mL HEPES buffer contained in a sample vessel to reach a concentration of 2 mM Zn^{2+}. The time of analyte addition is highlighted by an arrow. From previous experience [11] (and confirmed below), 2 mM corresponds to an excess of analyte and will saturate the PAN sensitiser with Zn^{2+}, *i.e.* all PAN molecules are involved in a chelate complex. We find that V_{out} responds immediately, and approaches a new equilibrium in a near-exponential approach within ~200 seconds. Note the smooth character of V_{out} which contrasts to the noisy V_{in}, Fig. 1d. This is tribute to the Lock- In amplifier. The overall change of V_{out}, ΔV_{out} (max), corresponds to the maximum possible change of absorbance this fibre can display. We here find ΔV_{out} (max) = 0.448 mV. With our calibration $\Delta V_{out} / \Delta A$ = 13700 mV this corresponds to ΔA_{max} = 3.27 x 10^{-5}, which is comfortably detected with our evanescent wave sensor. Equilibration is faster when concentration is increased by only a small amount (see inset to Fig. 2).

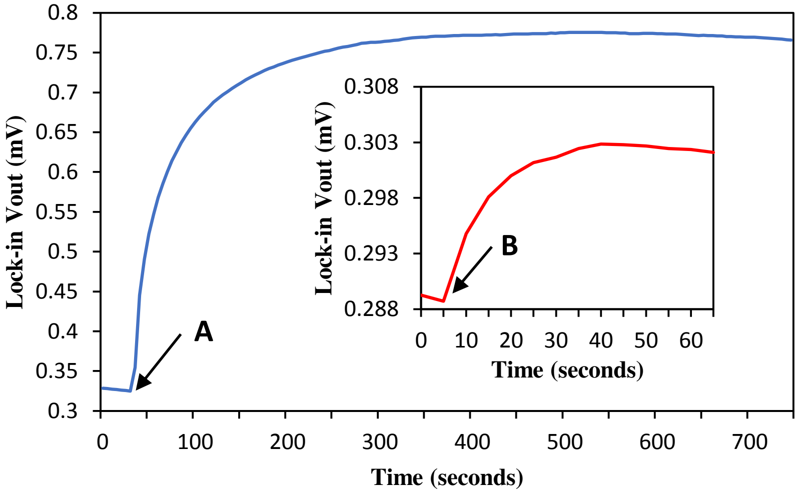


Fig. 2. Sensor response when an excess of Zn^{2+} (2 mM) was introduced (arrow A) into the vessel containing 8 mL HEPES buffer solution with a PAN coated fibre running through it. Inset: Response to a small concentration step (100 nM Zn^{2+}) at B.

For comparison (not shown here), we also tested a fibre sprayed from more concentrated PAN solution (10 mM *vs.* 1 mM). This led to larger ΔV_{out} (max) = 0.6 mV ($\Delta A_{max} = 4.4 \times 10^{-5}$) but required longer equilibration time (~ 400 seconds), both presumably due to the thicker coating. For a realistic sensor, we prefer to work with the faster response of the thinner coating from 1 mM spraying solution, as ΔV_{out} (max) = 0.448 mV is sufficiently large.

We have then explored the response of our evanescent wave sensor to small analyte concentrations, with a view to establishing selectivity, a response *vs.* concentration calibration and a limit of detection (LoD). Results are shown in Fig. 3.

On addition of Zn^{2+}, V_{out} shows a clearly visible and rapid response at a concentration as small as 50 nM increments. This confirms that our fibre optic evanescent wave sensor is highly sensitive to small amounts of Zn^{2+}. We limited our calibration to a maximum analyte concentration of 550 nM so that ΔV_{out} remains < 100 µV, about ⅕ of ΔV_{out} (max), to remain in the linear regime of the $\Delta V_{out}(c)$ characteristic. As control experiments, we have also characterised a non- sensitised fibre under addition of Zn^{2+} (orange), and PAN- sensitised fibres under addition of Ca^{2+}, Li^{+}, Ba^{2+}, and Na^{+} via their chlorides in the same concentration range as Zn^{2+}.

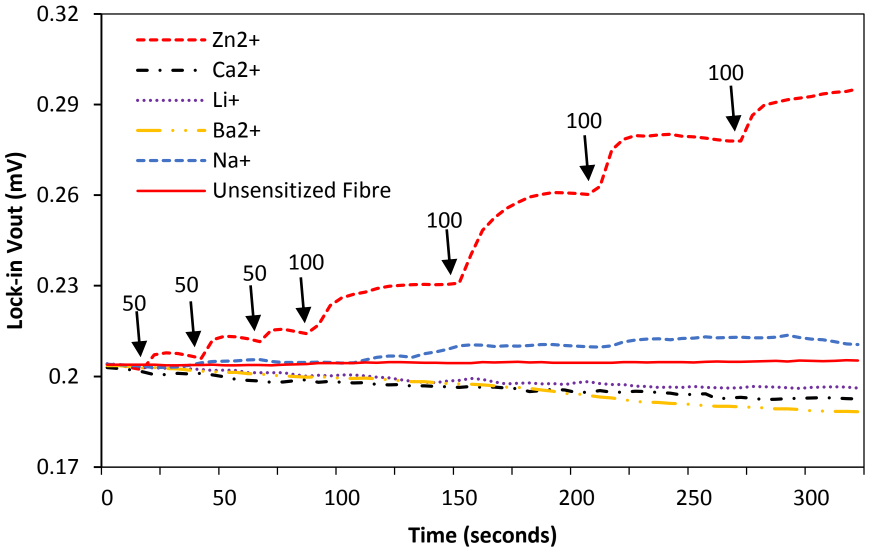


Fig. 3. Black: Lock-in output voltage V_{out} *vs.* time for PAN sensitized fibre under addition of Zn^{2+} in steps of 50 nM (initially) and 100 nM Zn^{2+} (for higher concentration), increments shown with arrows. Analyte was added in time intervals of 30s for 50 nM and 60 s for 100 nM. Orange: Control experiment with unsensitised fibre under Zn^{2+}. Also, control experiments for PAN- sensitised fibre exposed to Ca^{2+} (black), Li^{+} (purple), Ba^{2+} (yellow), Na^{+} (blue), added via their chlorides in the same concentration range as Zn^{2+}.

However, neither control experiment gives a strong response in V_{out}. This shows V_{out} response follows the selectivity of PAN, which chelates many (but not all) di- and trivalent transition metal and lanthanide cations (including Zn^{2+}), but not alkaline or earth alkaline metal cations [33]. Control experiments typically show a slow negative V_{out} drift, probably due to a small residual solubility of PAN in water, which is akin to the leaching of sensitiser from PVC membranes. For quantitative analysis, we have plotted sensor response *vs.* Zn^{2+} concentration, c, Fig. 4.

To evaluate LoD, we fitted a straight line $\Delta V_{out} = mc + b$ to the data in Fig. 4, and applied the widely used criterion for LoD [34],

$$LoD = 3\Delta b/m \qquad (1)$$

to find LoD = 54 nM from slope m = 0.192 μV/nM, and the error in intercept Δb = 3.512 μV. A previous report [29] on an optrode using the same PAN sensitiser dispersed in a PVC membrane gives a LoD of 1.53 μM. By introducing an alternative transducer we have achieved a 28- fold reduction in LoD for the detection of the same cation with the same sensitiser. When we extrapolate the linear ΔV_{out} (c) to its intersection with ΔVout(max) = 0.448 mV, we find this at c* = 2.33 μM, confirming 2mM is indeed an excess, as assumed earlier. c* = 2.33 μM suggests log K = -2 logc* = 11.3 for the equilibrium constant of the [PAN-Zn^{2+}-PAN] chelate complex.

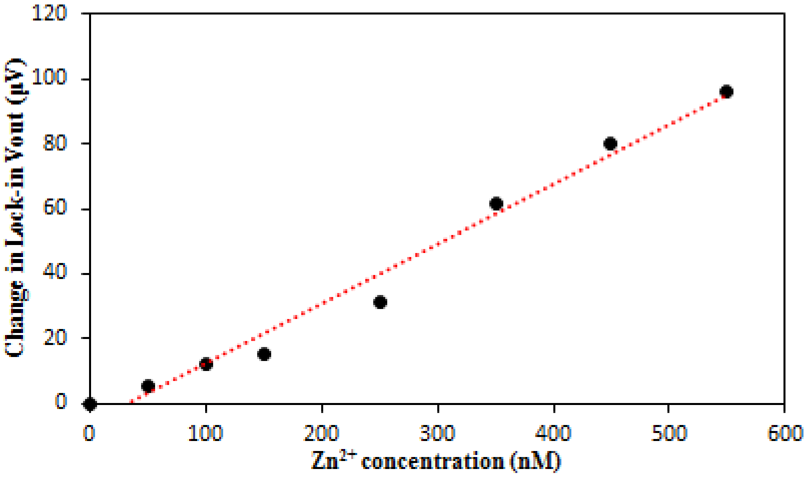


Fig. 4 Calibration graph for our fibre optic dual beam evanescent wave sensor when detecting Zn^{2+} with a PAN sensitised fibre. Data extracted from Fig. 3.

Finally, we studied the recovery of PAN- sensitised fibres. Fig. 5 shows V_{out} under a cycle of exposure to an excess of Zn^{2+} (as in Fig. 2) and subsequent recovery. To trigger recovery, we added an excess of the ion sequestration agent ethylenediaminetetraacetic acid (EDTA), which strongly chelates waterborne cations including Zn^{2+} and thus effectively removes previously added cations. V_{out} recovers over a period similar to the initial rise, eventually reaching a level slightly below the initial value, probably again due to some leaching. When a cycled fibre is washed in DI water, it can again be used for quantitative sensing, inset to Fig. 5.

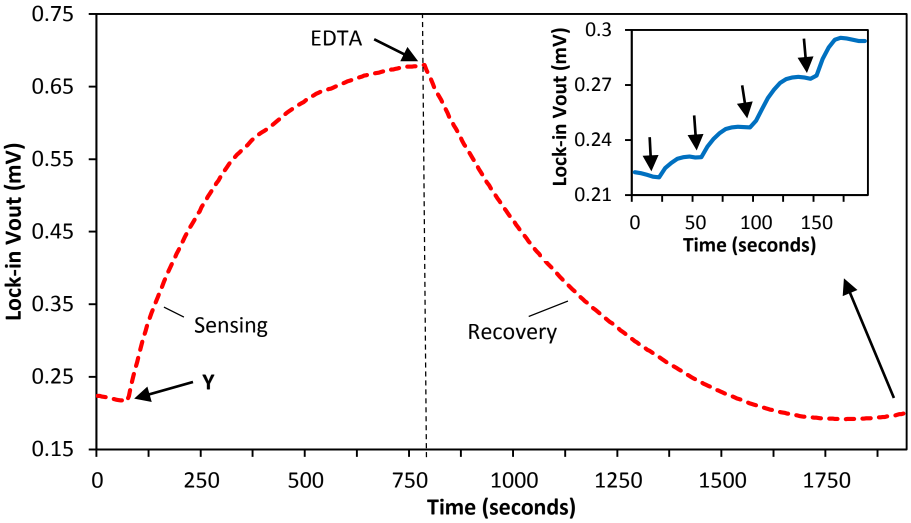


Fig. 5 Exposure / recovery cycle of PAN sensitised fibre to an excess of Zn^{2+}. Arrows indicate the introduction of Zn^{2+} (Y), and EDTA. Inset: Quantitative response of a 'recycled' fibre (cycled / washed in DI water) to Zn^{2+}. Arrows show addition of 100 nM Zn^{2+} each.

4. Conclusions

We have demonstrated a fibre optic dual beam evanescent wave absorbance meter for the detection of waterborne cations with a water insoluble organic chelating agent. We measured evanescent wave absorption with a bespoke fibre optic light balance that uses a sample- and a reference path to compensate for drift in light source intensity, and light intensity modulation with Lock-in measurement for low noise detection that is robust against ambient light interference. This instrument represents a new benchmark for absorbance measurements in evanescent wave fibre optrodes and establishes them as an alternative to PVC membrane or sol- gel matrix based optrodes that are traditionally used to mediate contact between waterborne cations and water insoluble chelating agents. We tested our instrument using the well characterised chromoionophore, PAN. We find a response for sub- micromolar cation concentrations with a LoD of 54 nM, 28 times lower than when same PAN sensitiser is used in a PVC membrane- based optrode [29]. Our instrument can be adapted to other chromoionophores simply by installing a different LED. For future work, we propose the use of macrocyclic chromoionophores as sensitisers, which are more cation- selective than chelators such as PAN.

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