Optical sensing system based on wireless paired emitter detector diode device and ionogels for lab-on-a-disc water quality analysis

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This work describes the first use of a wireless paired emitter detector diode device (PEDD) as an optical sensor for water quality monitoring in a lab-on-a-disc device. The microfluidic platform, based on an ionogel sensing area combined with a low-cost optical sensor is applied for pH (quantitative) and qualitative turbidity monitoring of water samples at the point-of-need. The autonomous capabilities of the PEDD system, combined with the portability and wireless communication of the full device, provide the flexibility needed for on-site water testing. Water samples from local fresh and brackish sources were successfully analysed using the device, showing very good correlation with standard bench-top systems.

Keywords: lab-on-a-disc, PEDD, colorimetric analysis, pH, turbidity.

Introduction

Water is an essential resource for living systems, industrial processes, agricultural production and domestic use. The quality of the environment in which we live influences a range of sectors including the general economy, and personal health and well-being.[1] In spite of the significant efforts to improve water quality in recent years, more than one in six people worldwide – nearly 900 million – do not have access to safe drinking water.[2]

These problems highlight the importance of adequate water quality monitoring in order to trigger early warning of contamination of water supplies. The need for reliable water quality information has never been greater - to identify current and emerging problems of water pollution, and to assess long-term trends and

environmental impact of housing developments, or changes in industrial/agricultural practices.

Traditional monitoring of water contamination is generally based upon manual in-situ 'grab' sampling followed by testing using lab-based methods. While this approach can provide some information regarding quality, it is not scalable in terms of the number of locations that can be sampled and the frequency of sampling. Consequently, even in developed countries, the vast majority of water bodies are monitored infrequently at a limited number of locations.[3] In contrast, *in-situ* measurements generated with autonomous instruments present a much more scalable model, enabling denser monitoring in terms of geographical locations and sampling frequency. This in turn can provide new information regarding natural processes governing the dynamics of chemical species behaviour.[4] In addition, various physical, chemical and biological processes can affect a sample from the time of collection to that of analysis, influencing its speciation, and causing significant uncertainty in the validity of aqueous speciation measurements.[5, 6, 7]

In view of the limitations of manual sample collection and subsequent laboratory analysis, there is great interest in *in-situ* water quality monitoring to ensure that aquatic areas are compliant with legislation. The challenge is to develop cheap and autonomous devices that can be used *in-situ*, with the capability to make the resulting data available remotely via web-databases, so that water quality can be monitored independently of location.[8, 9]

Miniaturisation of analytical devices through the advent of microfluidics is an important development for applications such as environmental monitoring as reflected in papers appearing in the literature. For example, Rohrlack *et al*. developed an opto-fluidic lab-on-a-chip that functions as a compact robust tool for the fast screening, real-time monitoring, and initial classification of algae. [10] Diamond and co-workers presented a microfluidic sensor for long-term monitoring of phosphate levels that incorporates sampling, reagent and waste storage, detection, and wireless communication into a compact and portable device.[11-13] An interesting approach to environmental monitoring was presented by Salazar *et al*., which developed a portable cell-based impedance sensor for toxicity testing of drinking water.[14] In addition, Ahn *et al*. presented an on-site water analyser capable of automatically performing long-term continuous sampling for heavy metals measurement using a continuous flow

sensing method with an array of disposable polymer chips.[15]

So far, on-chip water quality analysis have been mostly provided using standard lab-on-a-chip systems[16] and only a few examples have been reported in which centrifugal disc (CD) platforms have been used.[17, 18] For the last decade, such ''Lab-on-a-disc'' systems have been the focus of intense research, particularly for the development of diagnostic point-of-care devices[19] although some examples of applications for water quality analysis have begun to appear.[17] Centrifugal force has been used for sedimentation in numerous applications, both micro- and macro-fluidic. Since environmental samples can contain large amounts of suspended particulate matter, generally samples are routinely filtered prior to analysis. Employment of sedimentation/filtering directly on the disc therefore eliminates at least one sample preparation step leading to faster, simpler analysis.

In comparison to standard micro-chip-based systems, the use of centrifugal discs has several advantages in regards to portability, which is a key issue for *in-situ* water monitoring systems. Generally speaking, CD technology removes the need for pumps along with the interconnections required to driving fluids in traditional chips,[20] which allow the complete fluidic network and the employed assay to be contained within a single disc. Typically, fluid-pumping rotation speeds range from 300 to 3000 revolutions per minute (rpm).[20] Additionally, by employing centrifugal microfluidic technology, multiple experiments can be automated, enabling parallel processing and integration towards sample-to-answer systems. In comparison to the electro-osmotic pumping, centrifugal control of fluid movement is not dependent on pH, ionic strength[21] or chemical composition (in contrast to alternating current AC and direct current DC electro-kinetic pumping).[22] Finally, centrifugal platform technology replaces complex fluidic handling equipment and complicated interconnects, which helps keep costs to a minimum.[22]

While the centrifugal microfluidic platform is amendable for fluid processing, a complete analysis instrument requires the integration of sensing devices. The increased importance of environmental monitoring has spurred the need of developing inexpensive optical sensors capable of being combined with wireless communication capabilities.[23] The availability of broadly applicable optical components like light emitting diodes (LEDs) or photodiodes opens the potential of sensors to be widely employed in platforms for wireless network systems (WNSs). The key requirements

such as reproducibility, reliability, low power consumptions as well as sensitivity and selectivity are vital for scale-up and mass production of sensing devices, opening the potential for more widespread deployment.[24]

Commonly, optical system configurations combine LEDs as a light source with a charge coupled device (CCD),[25] a light wave multimeter[25] or a photodiode.[26] Mims III *et al.* demonstrated that a reverse-biased LED could also be employed as a very effective light detector.[27] More recently, Diamond and co-workers have described the so-called, 'Paired Emitter-Detector Diode' (PEDD), optical sensor with regard to configuration and application.[28] Worsfold *et al.* have successfully employed LED based chemical sensors for *in situ* monitoring of a variety of analytes with particular focus on phosphate[29] and nitrate/nitrite/ammonia.[30] An interesting approach to the photometric measurements based on PEDD for pH detection, enzymatic detection of urea, and evaluation of urease and alkaline phosphatase activities was presented by Koncki *et al.*[31] O'Toole *et al.* applied a paired emitter-detector diode for the detection of phosphate using the malachite green spectrophotometric method.[28]

In general, a PEDD consists of two light emitting diodes, one serving as the light source and the other, in reverse bias mode, as the light detector. The method achieves excellent sensitivity and signal-to-noise ratio (SNR) in comparison to the more commonly employed method of coupling a LED to a photodiode.[32] The low cost, small size, low power consumption, increasing spectral range coverage (247–1550 nm), intensity and efficiency, ease of fabrication and simplicity of the PEDD make it as an ideal optical detector for colorimetric assays.

The integration of low power, reliable wireless communications devices and *analytical* sensing (*e.g.* with chemo/biosensors) is an attractive proposition for the development of sensors working that can function collaboratively to monitor specific target parameters. In recent years, our group has focused its investigations on the incorporation of ionic liquids (ILs) in polymer matrixes, resulting in materials called ionogels. ILs have been widely studied because of their potential applications in many different fields like electrochemistry[33, 34] biochemistry[35] and microfluidics[36], due to their tunable hydrophobic and hydrophilic nature, chemical and thermal stability, low vapour pressure and high ionic conductivity properties.[37]

The incorporation of ILs into ionogels is a particularly attractive strategy in the field of sensing, since these materials, inherit all of the favourable IL properties whilst being in a solid, gel like structure.[38] For instance, Zhu *et al.* used phosphonium based

ionogels with a conventional chromoionophore for the detection of inorganic acids.[39] Topal *et al.* presented the increased selectivity of zinc phthalocyanines to pH when incorporated into imidazolium ionogels.[40] Benito-Lopez *et al.* presented for the first time a wearable, flexible and disposable barcode system based on phosphonium ionogels for real time monitoring of the sweat pH.[41, 42] An optode membrane capable of simultaneous recognition of Cu^{2+} and Co^{2+} ions in a single measurement has also been realised.[43]

In this manuscript we introduce the fabrication, characterisation and performance of a low-cost, wireless optical sensor based on a PEDD system, combined with a portable, multi-channel lab-on-a-disc platform based on a dye-ionogel sensing area. The platform is applied to *in-situ* monitoring of the pH (quantitatively) and the degree of turbidity (qualitatively) of river water samples. In addition to the easy operation and robustness of the sensor, the obtained results can be downloaded in remote locations and displayed in *real time.* The water quality results obtained with the prototype platform are in good agreement with parallel reference measurements, which provides a degree of validation for the platform and the analytical method employed.

Experimental

Materials

N-Isopropylacrylamide (NIPAAm, Sigma-Aldrich, Ireland), *N,N'*-methylene-bis(acrylamide) (MBAAm, Sigma-Aldrich, Ireland), 2,2-5 dimethoxy-2-phenyl acetophenone (DMPA, Sigma–Aldrich, Ireland), sodium dicyanamide (Sigma Aldrich, Ireland) and bromocresol purple (Sigma Aldrich, Ireland) were used for ionogel preparation. Tetrabutyl-phosphonium chloride $[P_{4,4,4,4}][Cl]$ ionic liquid was provided by Cytec Industries, Ontario Canada. The anion exchange reaction of $[P_{4,4,4,4}][Cl]$ with sodium dicyanamide was performed as described elsewhere,[44] in order to obtain tetrabutyl-phosphonium dicyanamide (abbreviated: $[P_{4,4,4,4}][dca]$). The IL was then purified thoroughly by column chromatography, dried under vacuum at 40 °C for 48 h, and stored under argon at 20 °C.

The colorimetric pH sensor utilised bromocresol purple pH dye (BCP) (Sigma Aldrich, Dublin, Ireland). Aqueous solutions were prepared using deionised water (Milli-Q). For the silanisation process acetic acid, methanol and 3-(trimethoxysilyl)propyl methacrylate were purchased from Sigma Aldrich, Ireland.

Oxidation of the PMMA surfaces was carried out using a Harrick Plasma Cleaner oxygen plasma. PMMA sheets (1500 μm) were purchased from Radionics, Ireland and 50 μm and 86 μm double-sided Pressure Sensitive Adhesive film (AR8890) from Adhesives Research, Ireland.

Yellow (590 nm) Surface Mount LEDs were purchased from Radionics, Ireland. These were operated under a stabilised constant current of 25 mA generated by an in-house made power supply. Arduino microcontrollers and Xbee modules were purchased from Sparkfun Electronics, Boulder, Colorado, USA. The in-house designed case and disc holder of wired and wireless detectors were fabricated using a 3D printer (Stratasys, USA), in acrylonitrile butadiene styrene co-polymer (ABS) plastic in order to protect the electronics and to minimise interferences from ambient light during the operation of the device. The printed parts were designed using ProEngineer CAD/CAM software package. The UV light source used for photo-polymerisation was a BONDwand UV-365 nm obtained from Electrolyte Corporation, USA (800 μW cm^{-2}). UV-Vis spectra and the emission spectrum of the emitter LED were recorded on a UV-Vis-NIR Perkin-Elmer Lambda 900 spectrometer. The bench-top pH meter (SevenEasy™ pH S20) was obtained from VWR International, Inc.

Lab-on-a-disc fabrication

To fabricate the multilayer centrifugal disc devices, poly-(methyl methacrylate) (PMMA) components were laser milled while double-sided, Pressure Sensitive Adhesive (PSA) was cut using a knife plotter machine (Graphtec, Japan). After manufacturing, the assembly was laminated together to create the final device (Fig. 1b). The fabrication of the microfluidic devices was carried out using a laser ablation system (Epilog Zing Laser Engraver, USA) and a cutter-plotter.

Design 1

In order to demonstrate the suitability of the PEDD device for integrated detection in a lab-on-a-disc, a first prototype was fabricated. The full characterisation of the integrated device was carried out using a five layer centrifugal disc with ten micro-channels (SI-Fig. 1). The upper chamber with inlet ports has an oval shape, with a length of 1.5 cm and a width 0.5 cm, whereas the bottom chamber, circle shaped, has

a diameter of 0.5 cm. The length of the micro-channel is 1 cm, with a total length of the microfluidic structure of 3.5 cm. The height of both chambers, which determines the light path length of the optical system, is 1.636 mm depth (PMMA layer, and PSA thickness together).

Design 2

The multi-parameter water analysis study was carried out using a CD containing seven large chambers with several sub-compartments for performing various functions, Figure 1. A PMMA upper section of height 1.5 mm, restricted by the thin PSA, creates the chamber containing an inlet port and a hole which facilitates air expulsion during rotation (Fig. 1b, A). The sieve opens over the middle microfluidic part (Fig. 1b, B), fabricated using a 1.5 mm PMMA and 50 μm PSA layer, which contains two rectangular reservoirs (4.5 mm x 7 mm and 1.55 mm depth), with photopolymerised ionogels: the reference, and the sensor with a pH sensing dye, bromocresol purple. Finally, the microfluidic area tapers to a bottom chamber of height 86 μm (Fig. 1b, C). Both, the upper and bottom chambers, contain horizontal laser milled lines which aided in visual inspection of collected particulates.

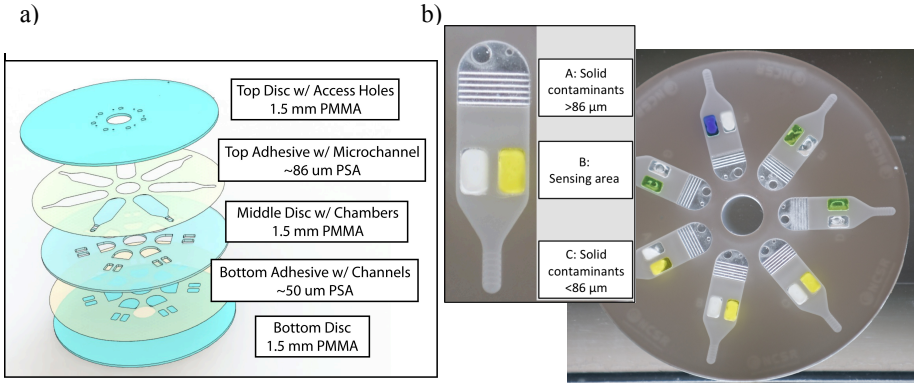

Fig. 1. a) Scheme showing the assembly of the microfluidic CD consisting of poly(methyl methacrylate) and Pressure Sensitive Adhesive layers. The plastic layers contain the chambers, whereas the adhesive layers contain the fluidic channels, b) picture of the Lab-on-a-disc device with a zoom of the fluidic channel with the sensing area; white (reference region) and yellow (ionogel sensor).

Ionogel pH sensing area fabrication

The sensing areas are based on ionogels consisting of poly(*N*-isopropyl-acrylamide) [x] and *N,N'*-methylene-bis(acrylamide) [y] cross-linked polymer in the ratio 100 (x):5 (y) in which the ionic liquid [$P_{4,4,4,4}$][dca] was entrapped into the polymer matrix.[45] Figure 2 presents the chemical structure of the polymer, Fig. 2a, the ionic liquid, Fig. 2b, and the dye, Fig. 2c, used in this study when photopolymerised in the PMMA/PSA reservoirs.

To facilitate ionogel stability in the disc, the PMMA surface in the reservoirs was chemically treated to facilitate covalent bonding of the ionogel. Firstly, the surface was oxidised in an oxygen plasma chamber for 60 sec, and then each reservoir was filled with 60 µl mixture of water at pH 3.5, methanol, and 3-(trimethoxysilyl)propyl methacrylate in the volume ratio 24:10:1. The silanisation step was adapted from a previously published protocol presented in the reference [46]. After 2 h, the reservoirs were rinsed with methanol and water several times and dried under nitrogen. The ionogel solution was prepared by adding the NIPAAm monomer, MBAAm crosslinker, and DMPA photo-initiator (molar ratio 100:5:3, respectively) to the ionic liquid (0.7 ml, 40 ºC for 20 min). This mixture was used to prepare an unresponsive reference (ionogel without pH dye) version of the sensor. The pH sensitive ionogel was obtained using the same mixture but with BCP dye (concentration 6 x 10^{-3} M or 10^{-3} M) dissolved in the IL before the addition of monomers and photo-initiator. Polymerisation of the reference and pH sensitive films was performed using a UV irradiation source (λ = 365 nm) placed 8 cm from the solution (UV intensity 10 mW cm^{-2}). When polymerisation was complete, the resulting ionogels were washed with water to remove any un-polymerised monomer and the excess ionic liquid.

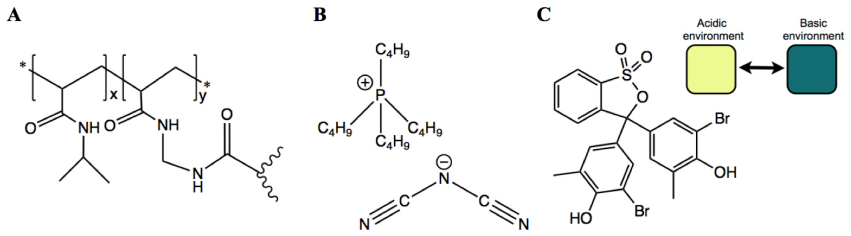

Fig. 2. a) *N*-Isopropyl-acrylamide and *N,N'*-methylene-bis(acrylamide) crosslinked polymer in the ratio 100(x):5(y) b) ionic liquid tetrabutylphosphonium dicyanoamide $[P_{4,4,4,4}][dca]$, c) bromocresol purple dye showing typical colour changes in acidic and basic environments.

Concentration of the dye within the ionogel matrix

The effect of BCP concentration on the sensor response was studied by preparing two series of ionogels with BCP concentrations of 6×10^{-3} M and 10^{-3} M. Both ionogels were exposed to buffer solutions and the colour dependent discharge time was recorded for 15 minutes using the PEDD detector. The concentration of the dye that provided the faster detection time, 15 min, *i.e*. when the relative slope of the signal was found to be less than 2 % for 1 min, was 6×10^{-3} M. Therefore, 6×10^{-3} M of BCP dye was adopted throughout all remaining experiments. An interesting point is that the polymerisation time required for the ionogel formation was shorter in the formulation containing the lower BCP concentration, at 25 min for 1 x 10^{-3} M, and 40 min, for 6 x 10^{-3} M. Moreover, no significant photobleaching was observed after exposure to the UV source for 40 min.

PEDD optical detector system

The PEDD detector consists of two pairs of Surface Mount LEDs (for reference and sensing regions), placed above and below the sensing area of the disc (Fig. 3a). One LED in each pair acts as the light source while the other is reverse biased, acts as a detector, as previously reported.[47, 48] Briefly, the detector LED in output mode was charged up to 5 V for 100 μs and then switched to high impedance input mode. Light from the emitter LED generates a photocurrent in the reverse biased detector LED, resulting in discharge of the capacitance based voltage from an initial value of 5 V (logic 1) to a present value of 1.7 V (logic 0). In order to provide a stable +5 V source to drive the circuit and LEDs, a voltage regulator running from a 9 V battery was employed. After passing through the microfluidic device, the observed light intensity is related to the discharge time of the acquired charge in the device[49]. The detector signal was captured using HyperTerminal software, saved as a text file and then analysed using MS Excel.

a) b)

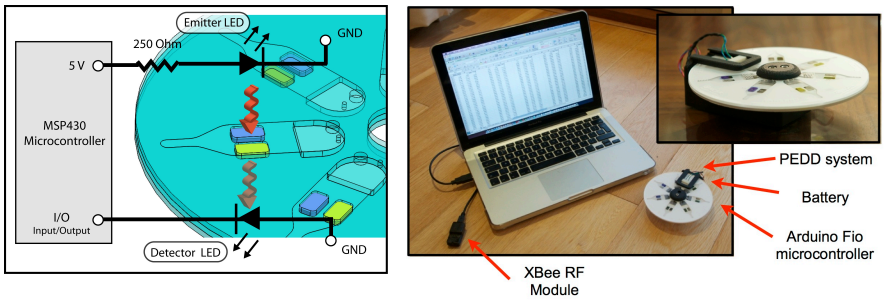

Fig. 3. a) Scheme of circuit used for the PEDD system. b) Prototype of the PEDD centrifugal microfluidic system.

A lithium polymer battery serves as the prototype power source and a USB/XBee socket is available to transmit data wirelessly to a laptop in real time via Bluetooth as shown in Fig. 3b (top). The PEDD system is integrated into an in-house generated 3D printed arm-like structure to ensure good alignment of the LED emitters and the LED detectors with the sensing and reference regions, Fig. 3b. Moreover, the PEDD detector can be slipped through the x-axis of the arm providing an extra degree of flexibility of the system. After spinning, the disc is transferred to a stand that provides free rotation and ensures that the PEDD detector addresses the sensing/reference regions in a reproducible manner.

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Optical characterisation of the PEDD detector in the lab-on-a-disc platform

The design 1 of the microfluidic platform was used to characterise the PEDD detector using different concentrations of aqueous solutions of BCP at pH 6.5. For comparison, UV-Vis spectra of the same BCP solutions were also obtained. A series of dilutions (1×10^{-3} M to 2.5×10^{-6} M in water) of BCP were also examined with the PEDD system by placing 10 μL of the solutions in the sample reservoirs of the CD,

and subsequently spinning to load the fluids into the testing regions. The resulting signal was measured continuously for 30 seconds. The sampling rate under this protocol is *ca.* 1 point per second.

Ionogel pH sensor calibration

To examine the behaviour of the pH-sensing ionogel, the pKa of the dye incorporated in the ionogel was determined. pH measurements of six buffer solutions with differing pH values (range 4-8) were carried out using the design 2. Solutions were placed sequentially in the sample reservoirs and spun at 1500 rpm for 5 min, in order to drive the liquid to the sensing area of the disc, where the photopolymerised ionogels were integrated as previously described. After 15 min the ionogel was fully hydrated and a stable and homogeneous colour was obtained.

Analysis of real samples

Water samples were collected from nine different locations on the Tolka River, Dublin, Ireland. 100 μL volumes of the samples were pipetted into the sampling ports the disc spun at 1500 rpm. Solids in the samples were retained in the upper chamber and/or accumulated in the bottom chamber according to their size, as mentioned before. The analytical measurement was carried out using the PEDD detection system in a dark environment, to reduce external light interference. The light dependence discharge time of detector LED was measured continuously for 30 s. The emitter LED was set to give 1 ms pulses of light as the light source for the absorption based measurements. The sampling rate under this protocol is *ca.* 1 point per second. In order to provide reference data, samples were also measured using a standard pH-meter, and turbidity was examined by UV-Vis spectrometry (% Transmittance).

Results and Discussion

PEDD lab-on-a-disc device

A centrifugal microfluidic platform was chosen for water quality analysis and

monitoring because fluid manipulation required a minimal amount of instrumentation. Additionally, multiple parallel fluidic assays can be integrated within one disc structure, enabling parallel processing of different samples, minimising costs and reagent consumption as explained in the introduction section.[22] The fabrication of the centrifugal platforms based on the milling of the PMMA layers and cutting of the adhesive layers, followed by the lamination step, was simple and straightforward. Moreover, the designed features could easily be adapted for mass production processes such as injection moulding.

Colorimetric disc-based detection has been previously used for clinical applications to detect biochemical markers such as calcium, creatinine, glucose, electrolytes and various blood protein panels[50], and also for analysis of chromium VI and nitrites in environmental water samples.[17] The integration of colorimetric detection using the PEDD system within the centrifugal platform presents significant advantages for lab-on-a-disc technology, as it can facilitate the integration of on-line, wireless and *in-situ* rapid measurements due to its inherent non-contact mode of operation. The autonomous capabilities of the system, combined with the portability and wireless communication, provide the flexibility needed for on-site water monitoring.

The present platform design enables simultaneous pH and turbidity measurements, which provides useful information on the management of the water during a treatment process and hence the quality of drinking water on the point-of-side. Although these parameters are not a risk to health, they indicate that corrective action and investigation is required before it becomes a potential risk. For example, elevated levels of turbidity have been shown to be associated with outbreaks of *Cryptosporidium* (Carlow, Ireland, in 2006 and Galway City, Ireland in 2007).[51]

PEDD detector characterisation

The wireless paired emitter detector diode device consists of two light emitting diodes (LEDs), as previously explained. This system allows for the creation of a digital output directly without using an A/D converter or operation amplifier. The system

was chosen due to its excellent sensitivity and signal-to-noise ratio (SNR) as explained in the introduction,[32] in addition to its universal and tunable properties,[24] which makes PEDD an ideal low-cost optical detector for many colorimetric assays.

A yellow LED (λ_{max} = 590 nm) was used as the emitter as the emission spectrum of the LED efficiently overlapped with the absorbance spectra of bromocresol purple dye (SI-Fig. 2). At this wavelength, the acid form of this dye has much lower absorbance than its basic form, which absorbs the LED light more efficiently and will give optimal sensitivity for this colorimetric measurement. In addition, a yellow LED was also employed as the detector.

In order to examine the efficiency of the wireless paired emitter detector diode device, series of dilutions of BCP were measured using UV-Vis spectrometry for control, and then with the PEDD system, employing the design 1 disc. According to the UV-Vis spectra of BCP (SI-Fig. 3), a linear relationship between absorbance and dye concentration was found over the concentration range from 2.5×10^{-6} to 5×10^{-5} M (pH 6.5 of the solution, basic form of the dye). It should be noticed that higher concentrations were not accurately measured while lower concentrations were not detected. The calibration curve of BCP pH dye is presented in Fig. 4, for both optical systems. Results showed close correlation between the PEDD system and standard UV-Vis spectrometry with similar limits of detection (LOD) (2.5×10^{-4} M). However, the PEDD system showed slight improvement with a linear trend over a wider range of concentrations. The results of the absorbance analysis of different concentrations of BCP dye water solutions using design 1 platform showed the successful application of this system for colour and colour-based pH measurements and offered high sensitivity, enabling detection down to the sub micro-molar concentrations of the dye.

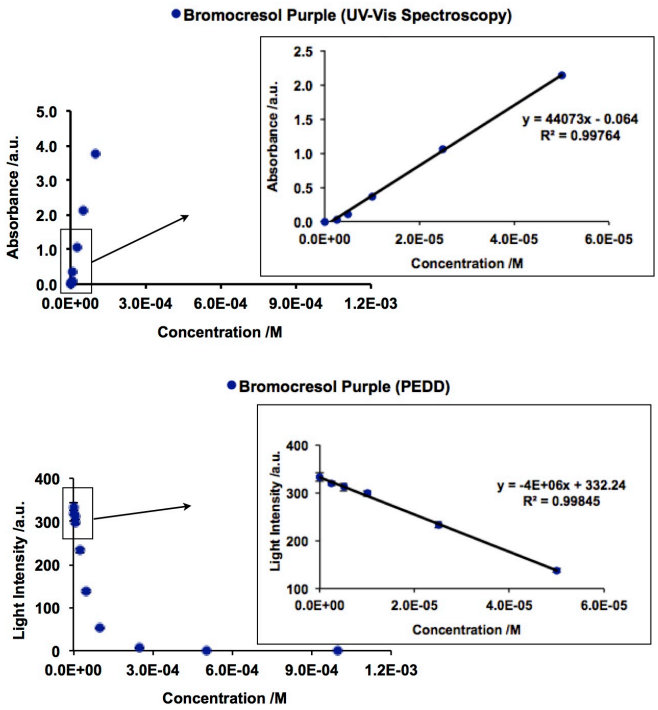

Fig. 4. Calibration curves of bromocresol purple pH dye in solution, n = 6, using a UV-Vis spectrometer (top) and the PEDD system (bottom), $L_{UV\text{-}Vis}$=1 cm, L_{PEDD}= 0.16 cm.[52]

Ionogel optical calibration using the lab-on-a-disc with PEDD detection

The use of the paired emitter detector diode (PEDD) device for colour and pH measurements has been reported previously in static solutions[49] and for flow analysis[53]. Here, for the first time we present the performance of a custom designed PEDD device for lab-on-a-disc applications. In the case of water pH analysis, the sensing function was provided by a pH indicator dye immobilised within an ionogel polymer matrix, which provides an excellent matrix for immobilising the dye (Fig. 1). As it was previously reported, due to ion-pair interactions between the pH indicator and the ionic liquid that forms the ionogel structure, there is no leaching of the pH dye during experiments, thereby providing improvement in robustness of the pH sensor[54]. In addition, the stability of the ionogel under harsh conditions (pH ranging from 0 to 14)[45] ensures accurate water quality monitoring over a wide pH range can be carried

out without degradation of the sensor matrix.

Further, a remarkable improvement on long-term sensor stability was achieved by ensuring covalent immobilisation of the ionogel to the surface of the PMMA substrate. This avoided the delamination of the swollen ionogel from the microfluidic device during sample analysis over time. The surface of the PMMA was treated with O_2 plasma and subsequently silanised using 3-(trimethoxysilyl)propyl methactylate. In this way, during the ionogel polymerisation, the monomers crosslinked with the free double bonds of the surface generating a covalent bond between the ionogel and the PMMA bottom channel surface.

Calibration of the chemical sensor

The pKa of BCP in the ionogel was determined using standard buffer solutions (Fig. 5). Depending on the pH of the buffer solution, the initial bright green ionogel colour changed to yellowish in a more acidic environment (pH = 4.0) and to dark green in a more basic environment (pH = 8.4) as depicted in the picture of the disc in Fig. 5b. The PEDD optical sensor was able to detect the colour changes of the ionogel that occurs at different pH values. The data obtained follow a sigmoidal curve, which is expected for this acid-base dye chemistry. The first derivative showed a pK_a value of 6.6 for the solid-state pH sensor. This indicates that immobilisation of the pH indicator dye in the ionogel, results in a shifting of the dye pK_a up to 0.3 pH units, in comparison to a pK_a of 6.3 reported in literature[55]. It was previously demonstrated that when pH indicator dyes are immobilised within solid gels, the micro-environment of the matrix shifts the pK_a of the dye slightly, on occasions by over 0.5 pH unit[56]. The observed pK_a value is also significantly influenced by the thickness of the gel, due to the increased diffusion constraint of the protons concerned and a change in dielectric properties of the ionogel[56]. From the pictures of the centrifugal platform in Fig. 1b it can be seen that a strong colour change is obtained using the *ca.* 0.8 mm thick ionogel sensor layer as this facilitates more efficient bulk proton diffusion and faster detection times.

The stability of the chemical sensor was demonstrated by performing several calibrations using the centrifugal platform (design 2). Calibrations showed good

repeatability with relative standard deviation (R.S.D.) typically within 2.7% (see errors in Fig. 5). This indicated that the pH indicator dye is stable over time (no leaching is observed during the measurements), and that the results are reproducible for different discs. Moreover the dye acid/base character is maintained within the ionogel since the dye is fully reversible from acidic to basic pH changes.

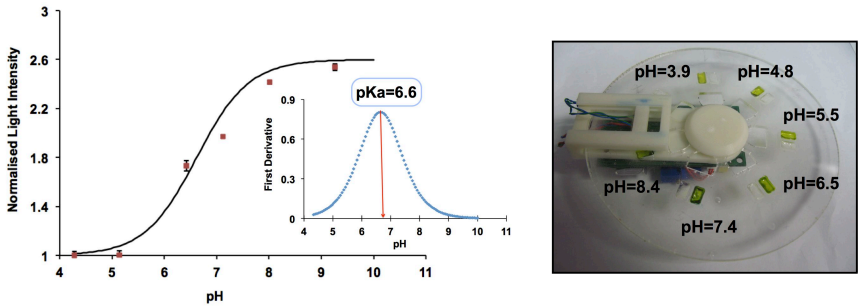

Fig. 5. Calibration curve of the sensing area of the microfluidic device using pH buffer solutions. (n = 3, error represents the average of light intensity values during data collection), and the first derivative with presented pK_a = 6.6 for the solid-state pH sensor. The equation used for the curve fit is as follows: y = 2.6-1.6/(1+exp((x-6.62)/0.49); sum of square residuals (SSR) = 0.07. The picture on the right side of the figure represents a CD platform with the ionogel/dye sensing area at different pH values, for calibration.

Application to environmental water analysis (pH and Turbidity)

Water quality analysis of samples from seven different locations of the Tolka River were carried out using the centrifugal disc (design 2). This river was chosen due to the report published in 2005 on a poor quality discharge of effluent and an associated fish mortality[57]. After collection, samples were loaded to the different upper chambers through the inlet ports of the disc. The disc was then placed on the motor stand and spun at 1500 rpm forcing the samples to the bottom chambers, covering the whole sensing area. The liquid and solid contaminants present in the water were transported through the microfluidic channel from the top to the bottom chamber during disc rotation (Fig. 6). After rotation, the sensing area that contains the ionogels/dye is fully covered with the sample and so the BCP pH dye changes colour according to the water pH.

Filtration

Light scattering of the solid suspended particles from the real samples results in an additional absorption in the detector. This problem can be solved by filtering the sample before detection, since it has been previously reported that the remaining particles lead to a large error during the colorimetric measurement if not filtered out.[58] Therefore, the design 2 of the centrifugal platform employed a filtration step (Fig. 6, yellow square). Due to the constriction generated in the upper chamber by the decrease in height of the micro-channel from 1500 μm to 86 μm (more than 94 %), solid particles larger than about 86 μm are trapped in this upper chamber, enabling an efficient sample filtration process. As a consequence, optical measurements carried out in the lower parts of microfluidic system can be substantially independent of the particles content of the sample, allowing for higher accuracy and reliability of analysis.

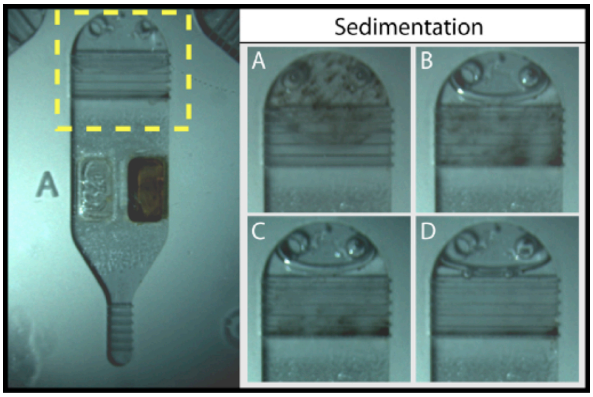

Fig. 6. Images of a channel of the CD during centrifugation at 1500 rpm. A) the upper chamber is filled with sample, then the disc is spun for two minutes and all the liquid is transferred to the sensing area (B-D). Particles of a diameter greater than 86 μm are accumulated in the upper chamber during the spinning process (B-D).

Turbidity

The results obtained with samples from the River Tolka are shown in Figure 6 A-D. The larger particles (>86 μm) were trapped in the upper chamber, whereas particles

smaller than 86 μm were accumulated in the bottom chamber. Fig. 7 shows a comparison of quantitative UV-Vis measurements (transmittance), for two samples (Fig. 7a), and a picture of the same two samples after qualitative on-chip analysis, (Fig. 7b). The low transmittance of sample no. 3 obtained by the UV-Vis spectrophotometer at 600 nm (Fig. 8a) correlates with the high amount of solid contaminants trapped in the upper chamber of the microfluidic system (Fig. 7b). In contrast, sample no. 7, which was relatively clean in comparison to sample 3 shows higher UV-Vis transmittance and a smaller amount of solid material accumulated in the upper filter region.

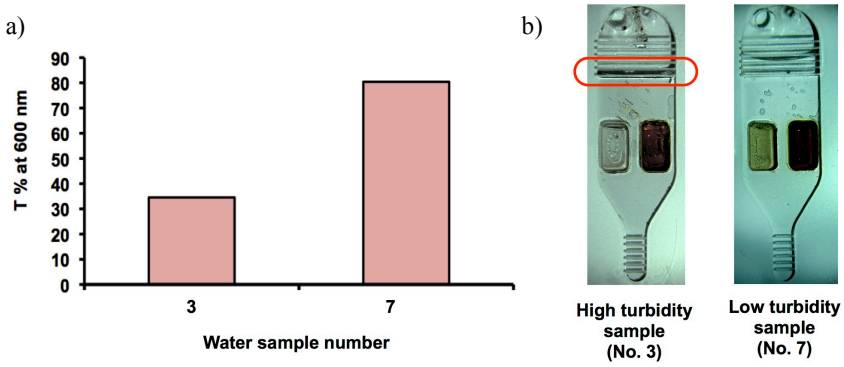

Fig. 7. a) UV-Vis spectrometer transmittance measurements of samples 3 and 7; b) pictures of the channels containing sample 3 (left, with particles accumulated in the highlighted region) and 7 (lower amount of solid material accumulated, right).

pH measurements

In the design 2 of the disc, the parallel microfluidic systems with pH dye/ionogel sensing areas are provided, allowing analysis of seven separate 100 μL samples. Measurements were carried out using the PEDD detector in a dark environment, to minimise external light effects, and the detector output monitored continuously for 30 seconds. As shown in the Fig. 8, an excellent correlation between pH results using the PEDD system and a standard pH-meter was obtained over the pH range 5-9. Our results also demonstrated that the ionic liquid anion $[dca]^-$, that is well known to behave like a Lewis base,[59] does not interfere with the response of the dye.

The results also indicate that the filtering step employed within the microfluidics allows for an accurate measurement even of turbid samples, thus

making the colorimetric detection substantially independent of the particle content of the real samples.

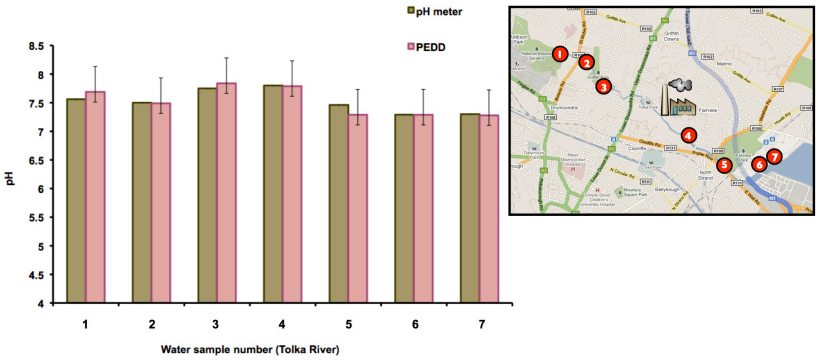

Fig. 8. Water pH analysis using a commercially available pH-meter and the PEDD lab-on-a-disc device at different locations of the Tolka River (Dublin, Ireland) (n=3). Google map picture of the different locations where samples were taken (right side picture).

Overall, the results obtained by the wireless, portable PEDD system demonstrate relatively good quality of the water samples, with regards to the turbidity and pH values. The results are within the range accepted by Environmental Protection Agency[60]. The data obtained with standard UV-Vis spectrometer, as well as those obtained with the lab-on-a-disc device, provide information on the improvement of the Tolka River water quality, which confirms the latest report showing significant reduction of the pollution levels[61].

At the moment, the spinning of the disc is performed using the bench-top spin stand setup, and once the fluids have reached the sensing areas, the optical system is attached to the centrifugal platform thus the detection takes place. Therefore, the incorporation of a remotely controlled motor for *in situ* spinning of the CD within the optical system, is currently under investigation. In addition, the on-chip turbidity measurement is performed through a simple visual inspection of the centrifugal platform, thus providing qualitative estimation of water turbidity. In order to improve the autonomous capabilities of the device, crucial for on-site water monitoring, our future work will also focus on the incorporation of a quantitative turbidity

measurement method based on the PEDD device.

Conclusions

A portable system for *in-situ* colorimetric water quality analysis has been developed. The device incorporates low-power detection coupled with wireless communication and power supply into lab-on-a-disc system. Integration of a wireless communication device allows data acquisition according to individual needs. Similar performance characteristics between the lab-on-a-disc device and standard UV-Vis spectrometer imply that the system is highly sensitive thus allowing for detection of several parameters at low concentration levels.

In general, this system shows the huge potential for the PEDD system to be a cheap and versatile alternative as point-of-care optical detector for lab-on-a-disc applications. We believe that this device will be of special interest in samples with a relatively high level of solid particles that could interfere with the optical analytical measurements.

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