

Low Cost Autonomous Sensors For Water Quality Monitoring

There is a growing need for low cost, remote sensing systems which can be deployed in situ in sufficiently large numbers to ensure that data on key water quality parameters is readily available. Microfluidic technology has great potential as a solution to the increasing demand for environmental monitoring, by producing autonomous chemical sensing platforms at a price level that creates a significant impact on the existing market. Our approach is to combine microfluidics with simplified colorimetric chemical assays; low cost LED/photodiode-based optical detection systems; and wireless communications. In order to drive down the cost of these devices, it is vital to keep the fluidic handling requirement as simple as possible, as complex multistage methods are expensive to implement as well as being less reliable in long-term deployments.

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The Grand Challenge

Monitoring and protecting the quality of our environmental waters is of major concern today. Our ability to effectively monitor the aquatic environment at remote locations is essential due to the increasing pressure on water resources from pollution, global climate change and growing demand. Environmental chemical sensors with microfluidics playing a key role have great potential as a solution to the increasing demand for environmental monitoring [1]. Subsequently, the data generated could be provided to all bodies of interest, be it monitoring agencies, local authorities or the general public, providing the much needed information for policy implications.

Presently, the challenges facing this ideal of in situ environmental monitoring are the multi-disciplinary approaches needed involving environmental science, engineering and material science. The cost of these platforms and the inability to “deploy and forget” due to limited long term stability and automated platform maintenance requirements are also major issues that inhibit this model [2] and has recently been described as the “Grand Challenge” posed for analytical scientists [3].

Approaches to water quality monitoring of nutrient levels like nitrate and ammonia have been the subject of much research over many years. However these well-established laboratory methods are making little progression into practical adoption for autonomous field based instruments. Cost is a major factor of this, mainly due to the need to incorporate expensive fluidic handling components, like pumps and valves.

Autonomous environmental sensors will offer a scalable model, measuring much more frequently at denser geographical locations and providing new information on the dynamics of chemical processes in natural water systems [4, 5]. The key to this idea of scalability is to produce these sensors as low cost as possible that can function reliable over a long period of time (ideally months -years) while still providing accurate data. The development of a rapid,

reliable, robust micro-scale system that could offer an alternative to the issues and challenges raised would be truly revolutionary in terms of the impact on existing market.

The Elements Of Miniaturisation

The basic building block of any reliable chemical sensor is the understanding and management of the fluidics. It is not sufficient or cost effective to use the majority of systems currently on the market that are based on macro-scale fluidics. Challenges that may be associated with these systems include dead volume within the system, consumption of power and the high volume of sample and reagents required leading to an increase in waste production [6, 7]. This is especially evident when one considers how to deploy and maintain sensors that are dispersed across a sizeable geographical area. The miniaturisation of analytical devices through the advent of microfluidics is an important development for future applications providing many advantages such as the small volumes of sample and reagent required, calibration procedures based on standard solutions can be easily automated and the optical detection takes place within the microfluidic chip which can be protected from fouling effects.

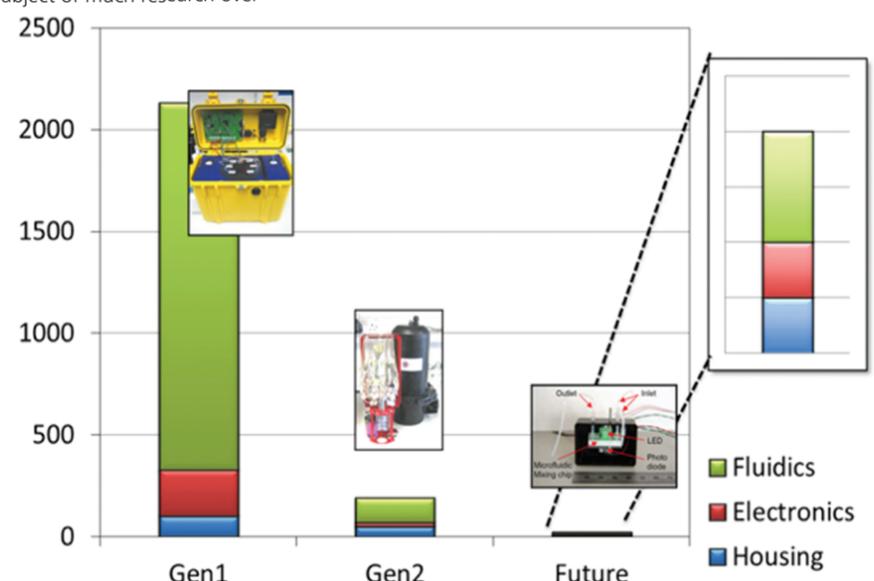


Figure 1 Component cost analysis of autonomous chemical sensing platforms illustrating fluidic handling (pumps and valves) as the largest contribution to cost falling less than 50% through the integration of microfluidics (Gen 2) and on all-polymer pumps and valves developed through fundamental materials science research (Gen 3). Source of figure [8]

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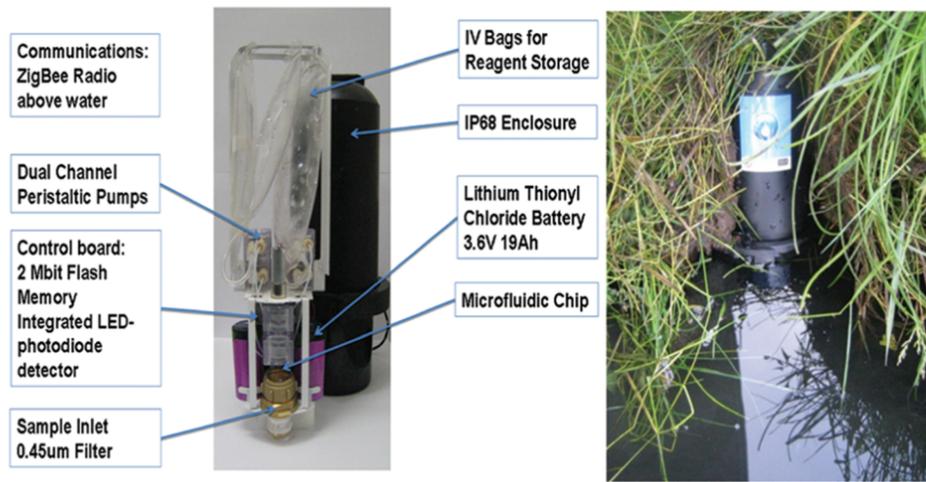


Figure 2 Phosphate analyser and system placed in situ in Broadmeadow Estuary. Data from the phosphate analyser and manual calibration samples (red).

It is apparent that the greatest contributor to the component cost is the fluidic handling [Figure 1]. Through the use of microfluidics (Gen 2) and 'future' platforms based on all-polymer pumps and valves developed through materials science research, the cost of these systems can be brought down considerably to less than 50% of the overall component cost.

Therefore, in order to drive down the cost of ownership of these devices, it is imperative to keep the fluidic handling requirement as simple as possible, as complex, multistage approaches are challenging and expensive to implement, as well as being less reliable in long-term deployments due to high maintenance costs.

The focus is on developing a low-cost detection platform for parameters such as phosphate, ammonia, nitrate and pH in water. By combining microfluidics with simplified colorimetric chemical assays; low cost LED/photodiode-based optical detection systems; and wireless communications (GSM, Wifi, zigbee) we can obtain very reproducible sample and reagent handling for the continuous operation of the system for a period of up to several months.

Water Quality Sensing Platforms

The autonomous microfluidic phosphate analyser is a compact and portable device capable of performing continuous monitoring for a period of 50-100 days at a frequency of 1 measurement per hour. The sensing system is based on the "yellow method", which is a colorimetric method that involves detecting the yellow colour produced when a reagent is mixed with an orthophosphate-containing sample absorbing strongly at a wavelength of 380 nm. The sensor implements a two-point calibration protocol using a blank solution (0 mg/L orthophosphate) and a standard orthophosphate solution, the concentration of which can vary depending on the particular site/sample in question. The two-point calibration is carried out for each sample measured and is vital in its ability to correct for changes in LED/photodiode response due to fluctuations in temperature, possible drift in response to detection system over time and possible change in sensitivity of detection system over time. Numerous field trials have been performed in both natural waters and wastewater treatment plants on the first generation. Over the past five years, over 10000 data points have been collected. The second-generation system involves a 10-fold lower cost as well as a significant size reduction and improved performance [9]. The analyser was placed in situ at Broadmeadow Water Estuary, Co. Dublin, Ireland for the period

22nd Feb 2012 - 2nd March 2012. This site was known to have high nutrient levels present due mostly to inputs from industry, agriculture and a wastewater treatment plant situated close by [10]. The analyser was employed to take a sample reading at 20 minute intervals. The sensor performed 350 autonomous measurements and 14 manual samples were collected for lab analysis and validation. This work has led the way for many important developments in further nutrient detection analysers.

The microfluidic analyser for pH and Chemical Oxygen Demand (MApCOD) project is one of latest projects in the development of a microfluidic platform for autonomous monitoring of environmental water quality. In this project pH is measured using a combination of pH indicators, optimised to give a colorimetric response over the pH range 4.0-10.0, which covers the range of pH values commonly encountered in monitoring of surface waters, drinking water and many wastewaters. Dual LEDs and a photodiode are used to measure light absorbance at appropriate wavelengths (430 and 570 nm). The responses of the two pH indicators are complementary, allowing a colorimetric response to be obtained over the pH range of interest. Calibration using a range of pH buffer solutions has shown that a linear response can be obtained by calculating the ratio of absorbance at the two wavelengths. Current focus is on optimising the performance of the system and carrying out field-based testing of the analyser system.

Nutrient Sensing Platforms

The first use of a direct nitrate analyser using chromotropic acid has been developed [11]. A simplified chromotropic acid method eliminating several steps previously associated with this method is employed in the platform. In a sulphuric acid medium, chromotropic acid reacts with nitrate ions and produces a characteristic yellow colour ($\lambda_{max} = 430 \text{ nm}$). The modified method allows for nitrate determination over a large linear range with a low limit of detection. Validation was achieved by analysing water samples from various sources including groundwater and trade effluent by the modified method and by the standard method (ion chromatography). The method was implemented onto an analysis platform shown in figure 3 incorporating a low cost paired emitter-detector diode (PEDD) as the optical detector.[12] The modified chromotropic acid method represents a rapid, simple, low cost technique for the direct determination of nitrate in water.

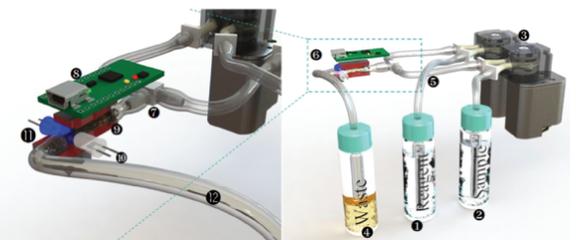
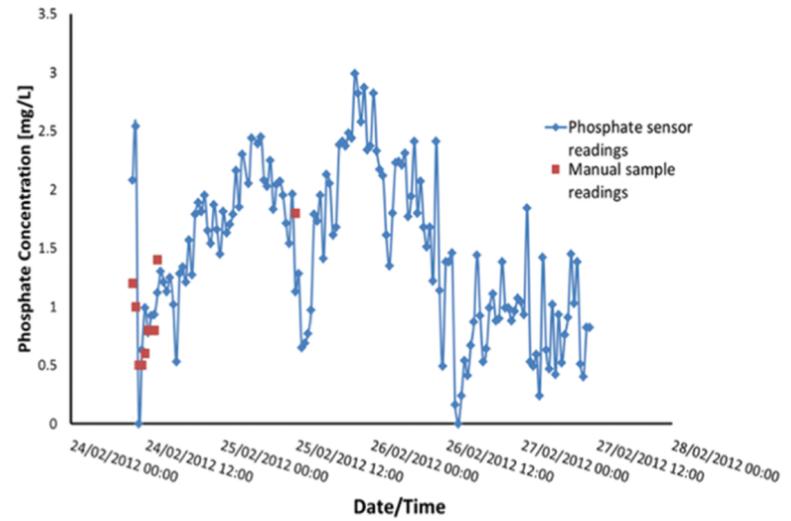


Figure 3 Nitrate Analyser and PEDD Detection System. (1) Reagent storage (2) Sample storage (3) Peristaltic micro pumps containing Santropene® tubing (4) Waste storage (5) Tygon® tubing (6) PEDD flow cell (7) Mixing junction (8) Wixel microcontroller with breakout board containing wireless serial link and data logger (9) Glass flow cell (10) Detector LED at 630 nm (11) Emitter LED at 430 nm (12) Waste line (Tygon tubing).

Nitrate sensors currently on the market predominantly use direct UV spectrophotometric screening, electrodes, or the cadmium reduction method, which in turn can be quite costly and/or prove difficult to implement due to the relatively intricate procedures involved and the limited detection ranges associated with various methods. There is therefore a major appeal to integrate this simple, direct method for the determination of nitrate into an autonomous platform shown in figure 4.



Figure 4 Field deployable platform for the detection of nitrate using chromotropic acid (1) robust and waterproof housing; (2) reagent and standard storage bags; (3) 12 V battery and control board; (4) microfluidic chip and optical detection enclosure; (5) peristaltic pumps containing Viton Tubing; (6) Sample inlet and filter.

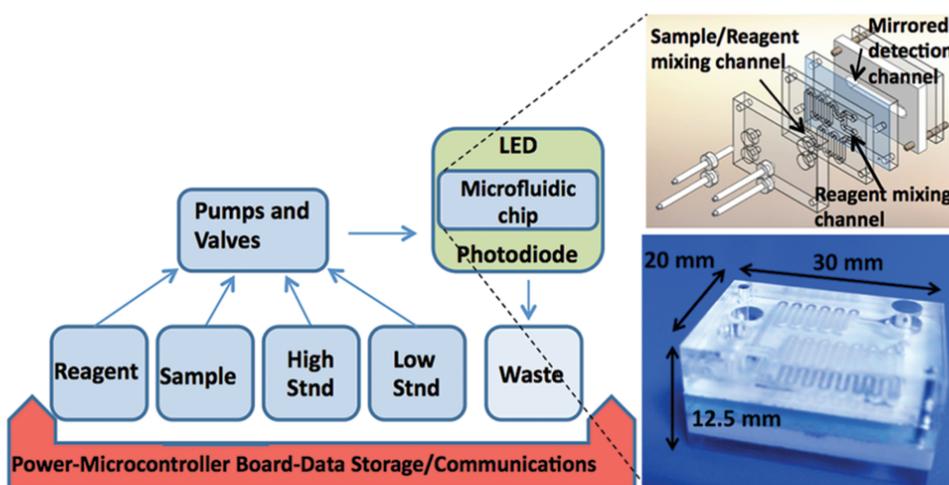
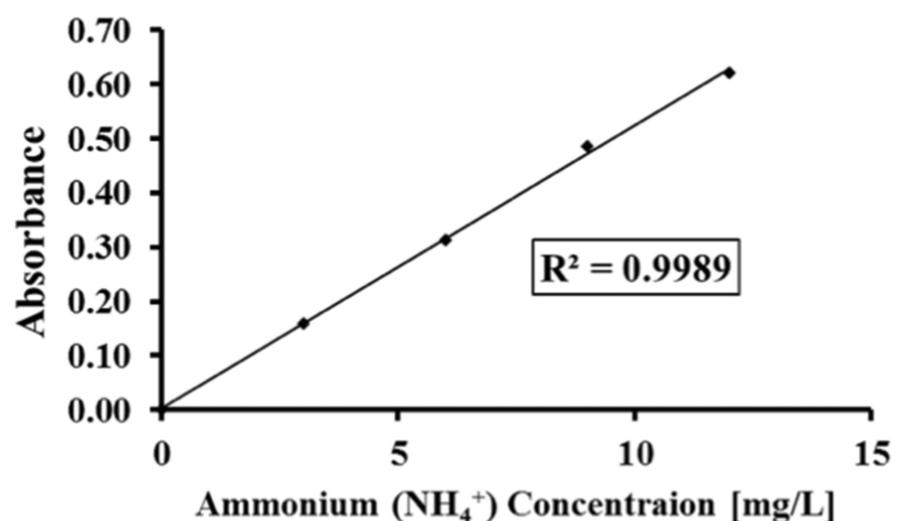


Figure 5 Schematic of the analyser and microfluidic chip. Calibration curve using the ammonia microfluidic chip from 0-12 mg/L NH_4^+ Berthelot complex. The standard deviations are represented as error bars ($n=3$).



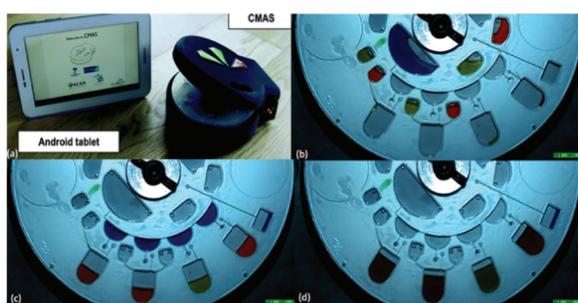


Figure 6 (a) Centrifugal Microfluidic Analysis System (CMAS) and Portable Android controller, (b) a multi nutrient test disc loaded with reagents to simulate sample and reagents before (c) the disc is spun on a motor at 1200 rpm to deliver the reagents to the detection chambers while the sample is delivered into four 100 µl aliquoting chambers (held back by dissolvable film valving systems) and finally (d) the spinning speed is increased to 2400 rpm to burst the dissolvable film valves and allow mixing of sample and reagents in the detection chambers prior to optical analysis.

It is now evident that in order to maintain and acquire a reliable and robust sensing platform, the fluidic handling strategies must remain as simple as possible. For the determination of ammonia, the Berthelot method was employed. In this method, an intensely blue coloured compound, indophenol, is formed in the presence of ammonia, hypochlorite and phenol. The most utilised variation of the Berthelot method incorporates a three step reagent process [13]. This method could prove problematic to implement in a low-cost fluidic monitoring platform due to the multiple stages involved. It was therefore vital to simplify the Berthelot method to allow for easy integration into an autonomous platform while maintaining satisfactory analytical results.

Figure 5 is a schematic of the microfluidic chip and illustration of the operating platform that was designed for the modified Berthelot reaction. The fluidic system comprises of sample intake, filtering unit, storage units for standards, reagents and waste and pumping system (comprising of pumps and valves).

The optical detection system consists of a 660 nm LED with a photodiode detector which enables an absorbance reading to be carried out on the ammonia/Berthelot complex. The control and data layer consists of a microcontroller which controls the operation of the pumping system and optical detector, a micro-SD card for data storage; and a Wixel for wireless communication using 2.4 GHz Radio. Power is provided by a 12 V lead acid battery for autonomous operation. The microfluidic chip shown in figure 5 was designed and built in-house, which is fabricated from UV-bonded layers of PMMA (poly methyl-methacrylate) into which a 0.5 mm channel has been formed by micro-milling.

Centrifugal Microfluidic Analysis Platform

The centrifugal microfluidic analysis system (CMAS) is a portable handheld wireless system developed for colorimetric analysis [14]. The device has been used for various applications including pH sensing [15], nitrite detection [14] and liver assay panel analysis [16]. The sample handling and fluidics are already prepared in a CD-like format, with appropriate micro-channels containing the required reagents and standards. The sample is placed within the device and a motor enables centrifugal testing

where measurements are made of the sample composition using a paired emitter-detector diode (PEDD). The information is transmitted wirelessly to the user's mobile phone or tablet computer, from which the user can control all instrument functions via an intuitive graphical interface.

Future Prospects

Conventional pumps and valves are the fundamental limiting factor in terms of miniaturisation and cost but remain essential to control liquid flow in the micro-channels. The scope of our future work is to explore how low cost polymer actuator valves might be incorporated into established microfluidic platforms. Our goal is the drive the component price of these current platforms at a price of approximately €200 down further to €20 by introducing biomimetic materials such as soft polymer actuators (artificial muscle) to control liquid flow [18]. We, and others, have already developed electro and photo-switchable polymer actuators [19] that can be fully integrated into microfluidic chips and used to control liquid movement. An interesting aspect is the incorporation of ionogels (the combining of ionic liquids within a polymer matrix) with the molecule- spiropyran resulting in a photoswitchable material. These ionogels show great promise as it does not require invasive stimuli. An ideal application for this gel is a microchannel within a microfluidic system as the opening/closing of the valve would be controlled by simply applying white light (Figure 7), thus replacing the conventional pumps and valves.

Concluding Remarks

The long-term deployment of chemical analysers is hindered by the lack of robust and reliable chemical sensing platforms. While much research is focused on the development of prototype sensors work must be achieved in transcending this research into the real analytical world. The progress in automated flow injection analysis (FIA) systems is prohibited by large sample volumes which results in high consumption of reagents and standards. The focus has now turned to microfluidics for the miniaturisation of these analytical techniques.[20] Through the miniaturisation of these devices and keeping the fluidic design as simple as possible, the overall reliability of the systems can be improved while reducing cost. The major focus is on real deployments with these modified approaches for in situ environmental monitoring.

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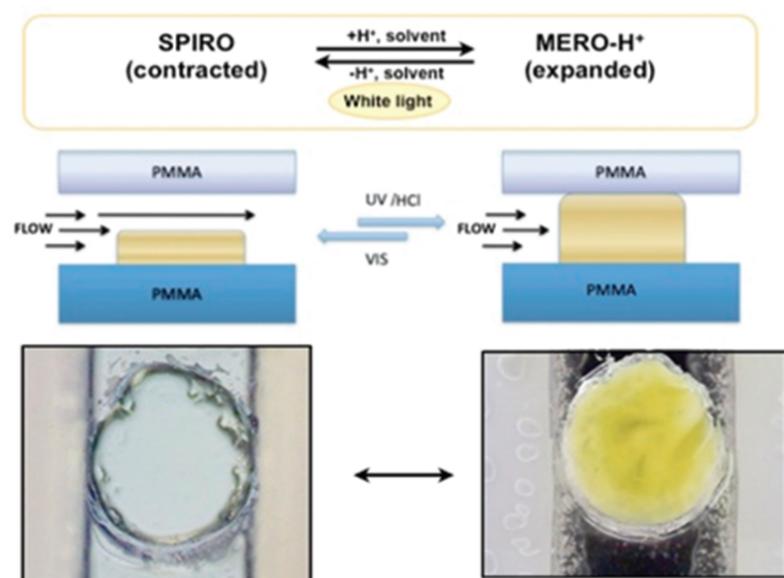
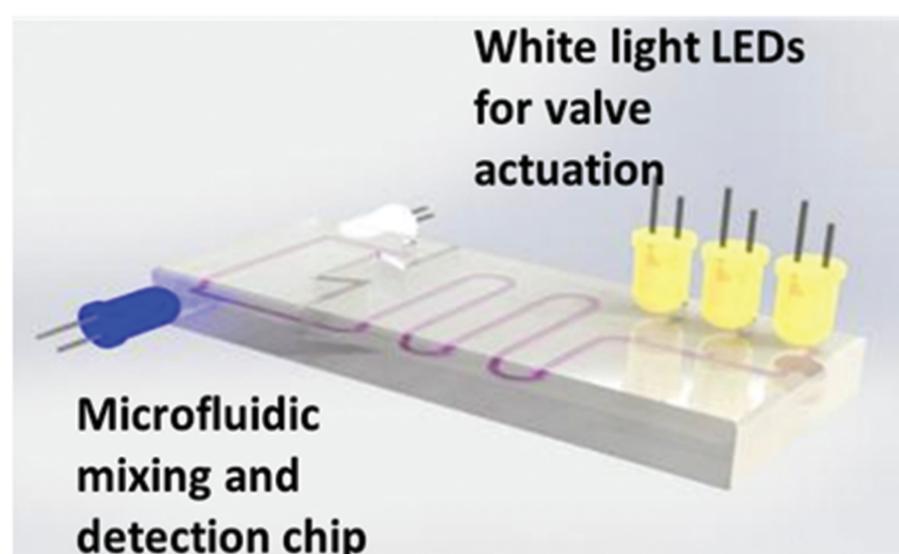


Figure 7 Scheme of the photoswitchable polymer matrix and schematic of the valve actuation, concept of integrated polymer valves within microfluidic chip.



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