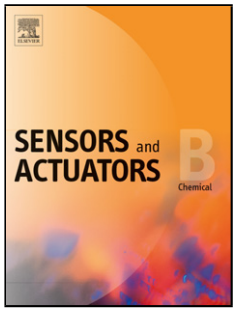

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Author: Gillian Duffy Ivan Maguire Brendan Heery Charles Nwankire Jens Ducrée Fiona Regan

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PhosphaSense: A fully integrated, portable lab-on-a-disc device for phosphate determination in water.

Gillian Duffy[a], Ivan Maguire[a], Brendan Heery[a], Charles Nwankire[a], Jens Ducrée[b] and Fiona Regan[a]

a Marine Environmental Sensing Technology Hub, Dublin City University, Glasnevin, Dublin 9, Ireland
b School of Physical Sciences, Dublin city University, Glasnevin, Dublin 9, Ireland

Corresponding author: fiona.regan@dcu.ie

Research Highlights

- Development of a chemical sensor for on-site phosphate determination in water
- System contains a centrifugal disc for automation of the colourimetric method
- A complementary system facilitates disc rotation and absorbance measurements
- Connection to a laptop via USB cable allows for live commands and data logging
- A long optical path length facilitated optimisation for low level PO_4^{3-} in water
- The system was applied to phosphate measurement in river water and WWTP samples

Abstract A portable, compact, centrifugal microfluidic system for the *in situ* quantitation of phosphate in water is reported. The device uses the ascorbic acid method, a colourimetric absorbance based assay, for phosphate determination. The integrated system consists of two components; the disposable centrifugal microfluidic disc and the complementary system. The microfluidic disc is designed to have similar dimensions to that of a compact disc, with a slightly thicker composition. Capillary active micro-channels are integrated internally, through which small and precise volumes of fluids can flow. Upon loading of the disc with a water sample and chemical reagents, the fluids can be moved through the disc using centrifugal force. This is created by rotation of the disc by the motor in the complementary system. The loaded fluids are then mixed due to rapid expansion and contraction as they are forced through the microfluidic channels and significantly larger reservoirs. Once mixing has occurred, this force will then drive the fluid into the optical detection zone. The low-cost optical detection system incorporated into the complementary system consists of an LED-photodiode transducing pair that measures the absorbance of light by the molybdenum blue complex formed at 880 nm. The total mass of 2 kg and dimensions of 20 cm x 18 cm x 14 cm make this system portable and convenient for analysis at the sampling site. The limit of detection (LOD) and limit of quantitation (LOQ) of this device were 5 and 14 $\mu g.L^{-1}$ PO_4-P, respectively. The linear range of 14 – 800 $\mu g.L^{-1}$ and sensitivity of 0.003 $AU.L.\mu g^{-1}$ make it suitable for analysing water bodies with low levels of phosphate.

Keywords Phosphate, optical sensor, centrifugal microfluidics, Lab-On-A-Disc, LOAD, water quality

Abbreviations limit of detection (LOD), limit of quantitation (LOQ), soluble reactive phosphate (SRP), lab-on-a-disc (LOAD), poly(methyl methacrylate) (PMMA), pressure sensitive adhesive (PSA), Waste Water Treatment Plant (WWTP), optical detection zone (ODZ), light emitting diode (LED), photodiode (PD).

1 Introduction

Phosphorus (P) is an essential nutrient for life. It is a growth limiting nutrient, which makes it an important parameter to monitor in water. [1] Elevated levels of growth-limiting nutrients lead to algal blooms. [2] These blooms can be a nuisance, however some algal species release toxins which are harmful to humans and animals. Aside from toxicity, decay of the large amounts of organic matter associated with algal blooms leads to hypoxic or anoxic waters, forming 'dead zones' where aquatic animals cannot survive. [3] These harmful algal blooms can have devastating effects on the local ecosystem, as well as on the fishing industry, water sports and leisure activities, and drinking water supplies.

Major sources of P entry into fresh water systems include fertiliser run-off from farmlands, and effluent from waste water treatment plants and industrial plants. It exists in many different chemical forms in water. [4] The simplest method for estimating bioavailable phosphorus in water is to analyse for soluble reactive phosphate (SRP). Orthophosphates are the most abundant forms of SRP at pH levels typically encountered in natural waters. [5, 6]

Phosphate cannot be measured directly in water, introducing the need for reagent based detection. A number of different strategies have been adapted for phosphate measurements on-site, including colourimetry, [7-12] electrochemistry [13-17] and fluorescence emission spectroscopy. [18-20]

Lab-on-a-disc (LOAD) devices are an ideal means for rapid on-site measurements as they allow for miniaturisation and automation of laboratory based analytical protocols, towards the development of inexpensive, portable and compact devices. [21] The use of microlitre volumes results in a reduction in reagent consumption, waste production and analysis times compared to standard laboratory protocols. This coupled with reduced cost, work flow and lowered sample contamination risk makes disposable microfluidic devices an attractive option for water analysis. [22]

Low reagent volume requirements improve portability of the system, as larger volumes of liquid reagents are cumbersome to transport, particularly when the sampling sites are difficult to access. Centrifugal microfluidics offers the added advantages of simplicity and low cost. In place of multiple microfluidic pumps, which are often expensive and require considerable power input, a simple motor is used for disc rotation, to generate a

centrifugal force which acts from the centre of the disc, radially outwards. [23] This centrifugal force propels fluid through the microfluidic channels.
The microfluidic platform for this system was fabricated from poly(methyl methacrylate) (PMMA) and pressure sensitive adhesive (PSA). It is rotated at ~8 Hz to create the centrifugal force for fluid manipulation. The on-board microfluidic architecture, including an air ventilation system for performance enhanced mixing of sample and reagents, also enables precise fluidic manipulation. Each disc has three separate analytical zones, allowing for three samples to be analysed before the disc can be disposed of. The ascorbic acid method for SRP determination was incorporated onto this device due to its high sensitivity compared to other colourimetric methods. A long optical path length of 75 mm was included in order to maximise absorbance signal, producing improved sensitivity and LOD.

Table 1.

There are currently few examples of LOAD devices for water quality analysis. Some parameters for water quality assessment that have been automated on-disc include pH, turbidity, nitrate, nitrite, ammonium, silicate and hexavalent chromium. [21, 24-27] These devices are compared in Table 1.

2 Materials and Methods

2.1 Chemicals

All solutions were prepared using ultra-pure water (Elga Maxima®, 18.2 MΩ) and ACS grade reagents purchased from Sigma Aldrich, Arklow, Ireland. Working standards were prepared by dilution of a 50 µg PO_4-$P.mL^{-1}$ stock solution, prepared from
potassium dihydrogen phosphate monobasic. A 0.032 M solution of ammonium molybdate tetrahydrate, a 0.004 M solution of potassium antimonyl tartrate and a 0.1 M solution of L-ascorbic acid were prepared. A 5 M sulphuric acid solution was prepared by adding 7 mL concentrated sulphuric acid (96%) to 50 mL of deionised water. The combined reagent was made freshly each day by mixing 5 mL sulphuric acid solution, 500 µL potassium antimonyl solution, 1.5 mL ammonium molybdate solution and 3 mL ascorbic acid solution. The volume ratio of water sample to combined reagent used for all experiments was 1:0.16. Complex formation time was 10 minutes from time of reagent addition.
A water sample was collected from the River Tolka in Dublin City, Ireland. This sample site was selected to act as a low level phosphate sample for the sensor. It was filtered through a 0.45 µm filter prior to analysis on the system. An effluent sample was collected at the effluent point of Ringsend Waste Water Treatment Plant (WWTP) in Dublin City. A 1 in 5 dilution of the filtered WWTP sample was measured on the system. This acted as a high level sample for the sensor.

2.2 Instrumentation

Reference measurements for the sensor calibrations and environmental samples were obtained using a Shimadzu mini 1240 spectrometer (Shimadzu Corporation, Japan). Samples were run in parallel with the LOAD device for comparison of performance. BrandTech® cuvettes (Sigma Aldrich, Ireland) were used for optical path lengths of 10 mm. Absorbance spectra were recorded using a VWR UV-1600PC UV-vis spectrophotometer (VWR, Ireland).
The cuvette holder and the PhosphaSense system were 3D printed using a Stratasys uPrint Dimension SE 3D printer (Tri-Tech 3D, United Kingdom) from Acrylonitrile butadiene styrene (ABS) polymer, enabling rapid prototyping. For the path length study, glass cuvettes (Spectro Service Ltd., United Kingdom) were used. The path lengths of these cuvettes were 2, 5, 50 and 100 mm.
The optical detection system consists of an OSRAM Opto Semiconductors light emitting diode (LED) (purchased from Radionics Ltd., Ireland) and a Vishay silicon PIN photodiode (PD) (part number: BPW24R, purchased from Radionics Ltd., Ireland). An 880 nm laser diode module (LM-104-E002, purchased from Roithner LaserTechnik GmbH) was used as an alternative light source for comparative purposes.

2.3 Disc design and fabrication

The centrifugal microfluidic disc was manufactured using PMMA sheets (Radionics™, Ireland), and PSA (Adhesives Research™, Ireland) respectively. It is made up of 5 layers, as shown in Fig. 1. The three PMMA layers, which contain the larger features, were cut using an Epilog Zing laser cutter (Epilog Corporation, CO, USA) (Fig. 1, yellow). These layers were adhered together using PSA, which contained the microfluidic channel features (Fig. 1, blue). This was cut using a Graphtec cutter plotter (Graphtec America Inc., CA, USA). The layers were assembled in a clean room, using a hot roll laminator (ChemInstruments, OH, USA) to activate the PSA.

Fig. 1. (Left) Rendered image showing each layer of the microfluidic disc, where (i) is a PMMA layer with air vents and fluid inlets; (ii) is a PSA layer with microfluidic channels; (iii) is a PMMA layer with microfluidic channels; (iv) is a PSA layer with an air ventilation system; and (v) is a base PMMA layer. (Top right) Rendered image of the microfluidic disc showing thickness; (bottom right) schematic of the microfluidic disc, which consists of a mixing reservoir (R) with inlets for sample and reagent loading, a microfluidic channel through which the fluids flow into the 75 mm long optical detection zone (ODZ), and an air vent (V) to release trapped air. The disc includes three alignment slots for precise optical alignment with the stage in Fig. 2.

The sample and combined reagent were added into the reservoir (R) of the disc, shown in Fig.1, using a micropipette with a combined volume of 600 μL, reaching the maximum capacity of the reservoir. On rotation of the disc at ~8 Hz, the sample and reagent were propelled through the microfluidic channels and into the 75 mm long optical detection zone (ODZ). As this detection zone filled, trapped air was released via a collapsible air ventilation system (V). This ventilation set-up was required to prevent the capture of air bubbles within the optical pathway. Air bubbles interfere with absorbance measurements, making their exclusion from the detection zone critical. The disc was allowed to gradually decelerate and was then aligned with the detection system using an alignment stage, which is shown in Fig. 2. The alignment pillars on this stage allowed for reproducible positioning of the detection zones in line with the LED-photodiode light pathway. Black acrylic paint was also applied to the PMMA each side of the detection window, to minimise light scattering and losses due to the disc materials.

2.4 PhosphaSense system design and fabrication

The 3D printed system was designed to directly complement the microfluidic disc. It was printed in 6 parts which were connected using screws. The system has a total mass of 2 kg, and dimensions of 20 x 18 x 14 cm. It contains a stage on which the disc is rotated by a motor. The optical detection system is configured for both LED-photodiode and LASER-photodiode pairing. Both pairings were carefully aligned to transmit light through the long optical detection zone of the disc. The transmitted light, at a reduced intensity due to absorption, then reaches the detection photodiode. A diagram of the PhosphaSense system is shown on the left in Fig. 2. The complementary system utilised a Wixel programmable module, (Cool Components, United Kingdom), to convert the outputted photodiode voltage into a digital signal, which can be interpreted and recorded by the end-user via ExtraPuTTYsoftware. The Wixel is also capable of receiving live user commands, which was exploited to control the on-board motor rotational speeds. The electronics were stored in a separate compartment below the stage. The device was designed to be direct current (DC) powered for future battery integration. The system currently operates using a 12 V AC-to-DC mains power supply in order to facilitate system optimisation within a laboratory-based environment.

Fig. 2. (Left) Rendered image of the PhosphaSense system where (a) is the lid for ambient light exclusion; (b) is the optical detection system; (c) is the motor; (d) is the microfluidic disc; and (e) is the compartment for electronics. (Right) Rendered images of the 3D printed stage components of PhosphaSense, where the top image shows the stage component of the system, with the motor top piece, and the bottom image shows how the optical alignment stage is fitted on top of the primary stage. The pillars on this stage line up with slots on the microfluidic disc shown in Fig. 1 to facilitate precise alignment with the detection system.

2.5 Optimisation of optical path length:

Optimisation of the path length for absorbance measurements within the microfluidic component was a critical step in platform development, to ensure that both maximum linear range and minimum LOD were achieved. To facilitate optimisation of this parameter using the LED-photodiode detection system, a custom-made cuvette holder was employed. The holder was designed to align the two light sources under investigation (an LED and a laser) with a detector (a photodiode for each light source). The experimental set up is shown in Fig. 3. The absorbance of a range of phosphate standards was measured at each path length, for each light source. The path lengths investigated were 2, 5, 10, 50 and 100 mm. The inside of the cuvette holder was painted black to minimise any light losses.

Fig. 3. Rendered image of the 3D printed cuvette holder with two light sources (an LED and a laser) and two detectors (photodiodes), precisely aligned for absorbance measurements over a range of optical path lengths.

2.6 Analytical method

The ascorbic acid method was adapted from reference 5 for use on this device. This method is based on the formation of a blue phosphomolybdenum complex with an absorption maximum in the near infra-red region of the electromagnetic spectrum. This method was selected from a range of standard analytical methods for phosphate measurement due to its high sensitivity, its ease of incorporation onto a microfluidic device, its stable product and its excellent reagent compatibility with the sensor materials. [5, 28]

2.7 Signal processing

The ADC outputs from the photodiode were converted to absorbance values using Eq. 1, where *blank* is the average ADC reading of a reagent blank (where n=3), and *sample* is the ADC reading of the sample under the same conditions.

Equation 1. $\mathbf{Absorbance = \log_{10}(\frac{Blank}{Sample})}$

Equation 2. $\mathbf{LOD = \frac{3.3(S)}{m}}$

The LOD was calculated using Eq. 2, where *S* is the standard deviation of the reagent blank (where n=3), and *m* is the slope of the calibration curve. The LOQ was calculated using 10 times *s*, divided by *m*.

3 Results and discussion

3.1 Calibration and evaluation of analytical performance

The calibration curve obtained using the fully optimised PhosphaSense system is shown in Fig. 4. This system displayed a linear response signal to phosphate concentration from 14-800 ug.L^{-1} PO_4-P. The LOD and LOQ values achieved were 5 and 14 µg.L^{-1}, respectively.

Fig. 4. Calibration curve obtained on the PhosphaSense system using prepared phosphate standards, where error bars show one standard deviation, with a slope of 0.003 AU.L.µg^{-1} and an R^2 of 0.9958.

The sensor's performance was compared to that of the same colourimetric method performed using a spectrophotometer. This comparison is shown in Fig. 5, with a more detailed comparison shown in Table 2.

Fig. 5. Correlation plot for the measurement of the phosphate standards on PhosphaSense (n=3) and on a spectrophotometer (n=3), where each point is labelled with the concentration in µg.L^{-1}. Error bars show one standard deviation in blue for PhosphaSense and in red for the spectrophotometer, with an R^2 value of 0.9915 and a slope of 4.71.

From Fig. 5, the close agreement between PhosphaSense and the reference spectrophotometric measurements demonstrates the sensor's excellent analytical performance. This is further highlighted by the comparison in Table 2. PhosphaSense exhibited a sensitivity that was five times greater than that of the spectrophotometric method. Although the standard deviation was higher for PhosphaSense, the LOD was half that of the spectrophotometric method, with a greatly improved LOQ. One drawback of PhosphaSense in this comparison was the diminished linear range in the upper region. This was due to the high percentage of light absorbed by the molybdenum blue species at higher concentrations. However, incorporation of a second, shorter optical path length through the width of the microfluidic disc would allow for measurement of these higher ranges without any changes to the microfluidic disc design. This could be easily incorporated into the next sensor prototype, as a second LED-PD pair located above and below the horizontal disc, measuring through the 2 mm path length of the disc.

Table 2

3.2 Application of PhosphaSense to phosphate determination in environmental water samples

The performance of the PhosphaSense system was demonstrated using water samples collected from two different water bodies, each of which represented a different phosphate level. This demonstrated the versatility of the PhosphaSense system for screening a variety of different water types. The river and WWTP effluent samples represented a low and a high phosphate level, respectively. The sensor output from these samples was compared to the spectrophotometric method, the results of which are shown in Table 3. It can be seen that the system measured both high and low level water samples with close agreement to spectrophotometric measurements. The standard deviation was low for both methods. Accuracy on PhosphaSense was good for both the Tolka and for the WWTP effluent samples, with a percentage error of 8% and 5%, respectively.

Table 3

PhosphaSense offers a range of advantages for on-site analyses. Its small dimensions and low mass make it portable and convenient to transport. Within 10 minutes, results from three different samples can be obtained from a single disc. No complex sample pre-treatment is required. A filtration of the sample was carried out prior to analysis. This is typically done on-site during sample collection regardless of analysis method. The sensor's very low component cost and ease of use would make it an attractive option for researchers, local authorities or legislative bodies, where expertise is not required for use. The power consumption of the system is relatively low, with a standby power use of 0.09 W and a maximum power usage of 2 W. The system would therefore operate with similar power consumption to standard small electrical appliances such as a battery powered alarm clock. This low level power consumption would also be beneficial in significant battery life. If the system was fitted with a chargeable 12 V battery with a modest 12 AH life, the system could potentially operate at maximum power for up to 72 hours, with full charge after 2-4 hours. Analysis on-site means that PhosphaSense is less prone to sample contamination and reduces work flow greatly, as the sample storage, transport and in-lab storage are removed from the analysis process. With the current microfluidic disc design, the combined reagent must be prepared freshly each day, as it has a shelf life of approximately 4 hours.[5] The poor stability of ascorbic acid in solution means that it must be prepared freshly each week. For the next generation sensor design, a sealed compartment will be incorporated on-disc to contain the ascorbic acid component in solid form. This would mix with the other two components of the combined reagent prior to the addition of the water sample, saving the user from cumbersome reagent preparation prior to each field trip.

3.3 Path length optimisation

The optical path length of the disc was optimised by comparing the LOD, sensitivity and saturation point (point at which 100% absorbance occurred) of five different path lengths, within the range investigated. The experimental set up is shown in Fig. 3. The results from this study are summarised in Table 4.

Table 4

*N/A indicates that the saturation point was not reached within the concentration range investigated.

From the data shown in Table 4, it is clear that there must be a compromise between the linear range and the LOD achieved by the sensor. Sensitivity increased with increasing path length, however for path lengths of 50 mm and above, the saturation point was reached. Therefore, a path length of 75 mm was selected as it allowed for minimisation of LOD within the working dimensions of the microfluidic platform. The linear range was diminished as a result, making this device more suited to measurements in water bodies where phosphate levels are typically below 800 $\mu g.L^{-1}$.

This study highlights the versatility of the system, whereby sensitivity can be selected for by designing microfluidic discs with a range of different path lengths. A long path length maximises sensitivity, making it best suited to measuring low levels of phosphate, while short path lengths allow for determination of high phosphate levels. A sampling site can be screened in order to approximate the phosphate range. The microfluidic disc with the predetermined optimal path length for this phosphate range can then be used for sample analysis.

4 Conclusions

A fully integrated, centrifugal, microfluidic optical sensor for phosphate determination in water has been developed. The use of a microfluidic disc was advantageous as it allowed the use of a long optical path length

for improved sensitivity, while also enabling low reagent and sample volumes to be used. The detection limit achieved by the standard spectrophotometric ascorbic acid method is 10 $\mu g.L^{-1}$ PO_4-P. [5] By adapting this method onto a microfluidic device, using a simple design to facilitate mixing and by including a long optical path length, a comparable LOD of 5 $\mu g.L^{-1}$ has been achieved. However, the device has a diminished linear range of 14 - 800 $\mu g.L^{-1}$, compared to the spectrophotometric method range of 150 - 1,300 $\mu g.L^{-1}$ PO_4-P. [5] This makes the system suitable for measurement of water bodies with low levels of phosphate. Future work will aim to incorporate a second absorbance measurement through the width of the disc, which has a short path length of 2 mm, thus extending the range of detection to the upper range. This addition will be included in the next version of the PhosphaSense system, making the system capable of measuring over a wide range of phosphate concentrations. The next prototype will also feature a lid compartment for storage of all electronic components, rather than underneath the fluidic system which can lead to damage from leaks or splashes.

The LOD, LOQ, linear range and sensitivity show the system's good analytical performance when compared with the same method carried out using a spectrophotometer in a laboratory. The PhosphaSense system offers boundless opportunity for further tailoring of the microfluidic network and modification of detection wavelengths to permit determination of a wide array of analytes of interest through robust colourimetric methods.

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Biographies

Gillian Duffy

Gillian Duffy B.Sc. is a final year PhD candidate at Dublin City University (DCU), under the supervision of Prof. Fiona Regan and Prof. Dermot Diamond. Her research is focused on the development of low cost, wet chemistry based optical sensors for water quality monitoring. Gillian was awarded a Naughton Fellowship from the University of Notre Dame, USA to complete this research. She received a B.Sc. (Hons) in Analytical Science in 2013 from DCU, and completed research on paper based microfluidic systems with electrochemical detection for separation and quantitation of electroactive analytes. She also received a Hamilton Research Scholarship in 2011 on microfluidic technologies under the supervision of Prof. Jens Ducrée in the National Centre for Sensor Research (NCSR) at DCU. Her research interests include analytical chemistry, method development, optical sensor development and technology for environmental and medical applications, and microfluidic technologies.

Ivan Maguire

Ivan Maguire, currently a research PhD student since 2014, is a member of the Marine and Environmental Sensing Technology Hub (MESTECH), Dublin City University (DCU), supervised by Prof. Fiona Regan. He studied Physics with Biomedical Sciences at the DCU and graduated top of his class in 2014. During his degree, he underwent a final year project which was aimed at the sorting and detection of circulating tumour cells (CTCs) by using the in-house developed, strategic microfluidic obstacle architecture designs, and was supervised by Dr. Charles Nwankire and Prof. Jens Ducrée. He continued his microfluidic research in the form of a PhD program sponsored by an FP7-funded called 'MARIABOX', SmartBay Ireland and MESTECH, DCU. His primary technical challenge is the development of a centrifugal microfluidic platform capable of detecting targeted marine pollutants, with other interests in the integration and automation of both marine and non-marine based monitoring systems.

Brendan Heery

Brendan Heery, (B.Eng, PgDip) is a Mechatronic Engineer, completing his PhD on Marine Sensing with Mestech, DCU. Brendan specialises in sensor instrumentation for chemical analysis, including optical and electrochemical systems. He is currently employed as an R&D Engineer by PalmSens BV in the Netherlands.

Charles Nwankire

Dr. Charles Ezenwa Nwankire is an Irish Research Council Fellow at University College Dublin, Ireland. He obtained his BSc and MSc degrees from St. Petersburg State Technical University, Russia; and PhD degree from University College Dublin, Ireland with international scholarships. He is internationally recognised for his work in biomedical engineering, material science and design technology. He is a co-inventor of 2 patents, published 1 scientific book, 3 book chapters and over 25 peer-reviewed research and review articles. For over 10 years, he has developed cutting edge technologies with leading institutions and multinational corporations including EMD Millipore USA, Medtronic Inc. USA, Alfa Laval Sweden, Suomen Karbonatti, Finland, etc. Dr. Nwankire has won awards in Science communication and Commercialisation in Life Sciences and has made poster and invited oral presentations at international scientific conferences. He has research interests in point-of-use devices and materials for biomedical and environmental monitoring.

Jens Ducrée

Dr. Jens Ducrée's main scientific research interests are in the fields of micro- and nanofluidic lab-on-a-chip technologies, underlying micro- and nanofabrication schemes, handling and processing of complex (bio-)fluids including blood and cell suspensions, detection technologies, instrumentation and system integration. The fields of application he has been involved in are cell research, systems biology, immunoassays, molecular diagnostics, integrated sample preparation, bioprocess engineering, water analysis, energy harvesting, microprocess engineering and polymer microfabrication. Dr. Ducrée has been very active in technology transfer, e.g. by engineering research tools for the life sciences, systems biology and biomedical, point-of-care diagnostic devices compliant with clinical environments, doctor's offices and resource-poor settings in home care and global health.

Fiona Regan

Fiona Regan, Associate Professor in Environmental Sensing since 2009, established the Marine and Environmental Sensing Technology Hub (MESTECH), DCU in 2010. She studied Environmental Science and Technology at the Institute of Technology in Sligo and graduated in 1991. After completing her PhD in analytical chemistry in 1994, and postdoctoral research in optical sensing in 1996 at DCU, she took up a position at Limerick Institute of Technology as lecturer in Environmental and Analytical Science. In 2002 Fiona returned to the School of Chemical Sciences, DCU, as a lecturer in analytical chemistry, in 2008 she became senior lecturer and in 2009 became the Beaufort PI in Marine and Environmental Sensing. Her research is in the area of separations and sensors, materials for sensing and anti-biofouling applications on aquatic deployed systems, including novel sensors and sensor networks and decision support systems. Fiona is Director of MESTECH and coordinates the Marine ICT SmartBay research under PRTLI V and the International SmartOcean Graduate Enterprise Initiative (ISGEI).

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Table 1. The LOD, linear range and attributes of centrifugal microfluidic water quality sensors with optical detection. [21, 24-27]

Author	Analyte	LOD	Linear range	Attributes	Comments
Czugala[21]	pH	$2.5x10^{-4}$ M (BCP dye)	$2.5x10^{-6}$ – $5x10^{-5}$ M (BCP dye)	Portable, yields results on-site, LOD comparable with lab methods	Low power requirements, low cost detection system
	Turbidity	N/A	N/A	Excludes particles from optical detection chamber	
Czugala[24]	Nitrite	9.31 µg.L^{-1} NO_2^-	0.2-1.2 mg.L^{-1} NO_2^-	Portable, yields results on-site, LOD comparable with lab methods	Low power requirements, low cost detection system
Xi[25]	Nitrate	0.16 mg.L^{-1} NO_3-N	0.16-5 mg.L^{-1} NO_3^--N	Multiple sample capacity on one disc	High power requirements, more expensive detection system
	Nitrite	0.05 mg.L^{-1} NO_2-N	0.05-5 mg.L^{-1} NO_2^--N		
Hwang[26]	Nitrite	0.008 mg.L^{-1} NO_2^--N	0.027-10 mg.L^{-1} NO_2^--N	Multiple analytes on one disc	High power requirements, expensive detection system
	Nitrate + Nitrite	0.05 mg.L^{-1} NO_3^-- N	0.07-10 mg.L^{-1} NO_3^--N		
	Ammonium	0.01 mg.L^{-1} NH_4^+-N	0.05-10 mg.L^{-1} NH_4^+-N		
	Ortho-phosphate	0.008 mg.L^{-1} PO_4^{2-} - P	0.024-1 mg.L^{-1} PO_4^{2-}-P		
	Silicate	0.19 mg.L^{-1}	0.79-100 mg.L^{-1}		
LaCroix-Fralish[27]	Nitrite	0.008 mg.L^{-1} NO_2-N	Up to 5 mg.L^{-1} NO_2-N	Calibration and multiple samples measured on one disc	High power requirements, more expensive detection system
	Chromium (VI)	0.03 mg.L^{-1}	Up to 5 mg.L^{-1}	Dry reagents stored on disc allow for single step analysis	

Table 2. Comparison of the analytical performance of PhosphaSense and the reference spectrophotometric method

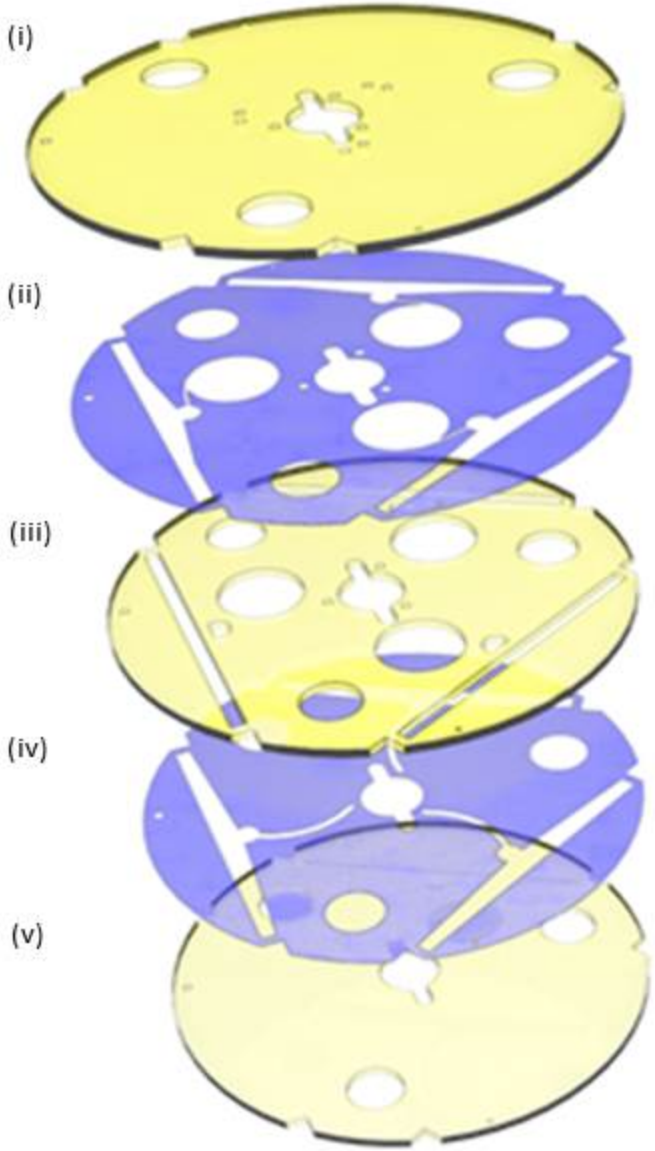
Analytical method	Path length (cm)	Slope ($AU.L.\mu g^{-1}$)	LOD ($\mu g.L^{-1}$ PO_4-P)	LOQ ($\mu g.L^{-1}$ PO_4-P)	Linear range ($\mu g.L^{-1}$ PO_4-P)	R^2
PhosphaSense	7.5	0.003	5	14	14-800	0.9958
Spectrophotometer	1	0.0006	10	150	150-1,300	0.9995

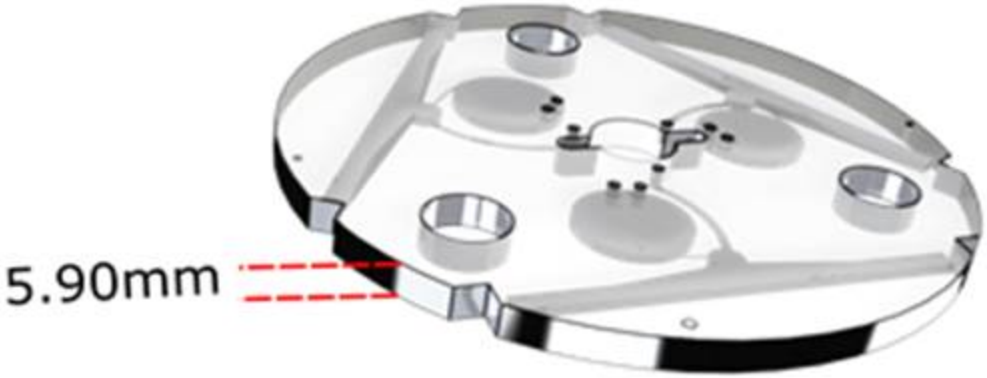
Table 3. Phosphate measurements from PhosphaSense (n=3) and the reference spectrophotometric method (n=3)

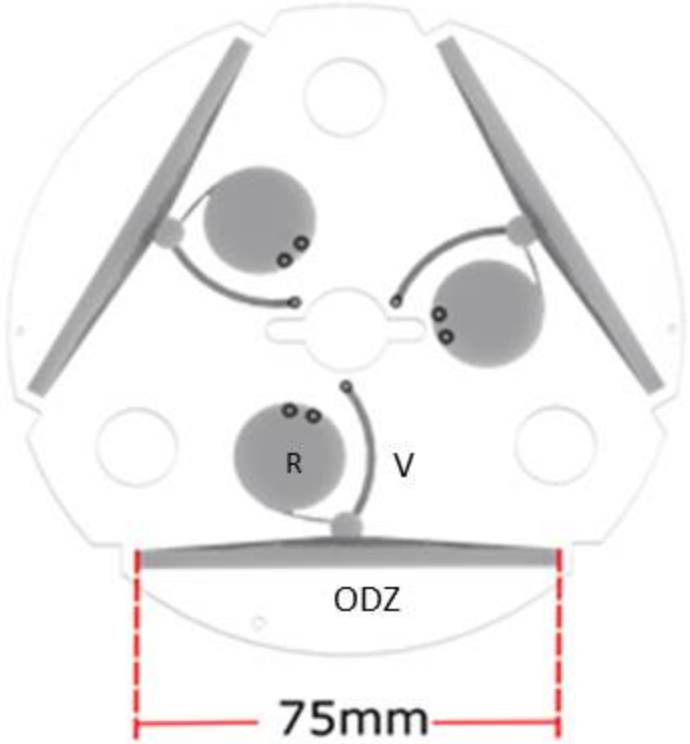
Sample ID	PhosphaSense (µg.L^{-1} PO_4-P)	Spectrophotometer (µg.L^{-1} PO_4-P)
Tolka	44 ± 3	48 ± 2
WWTP	620 ± 2	656 ± 1

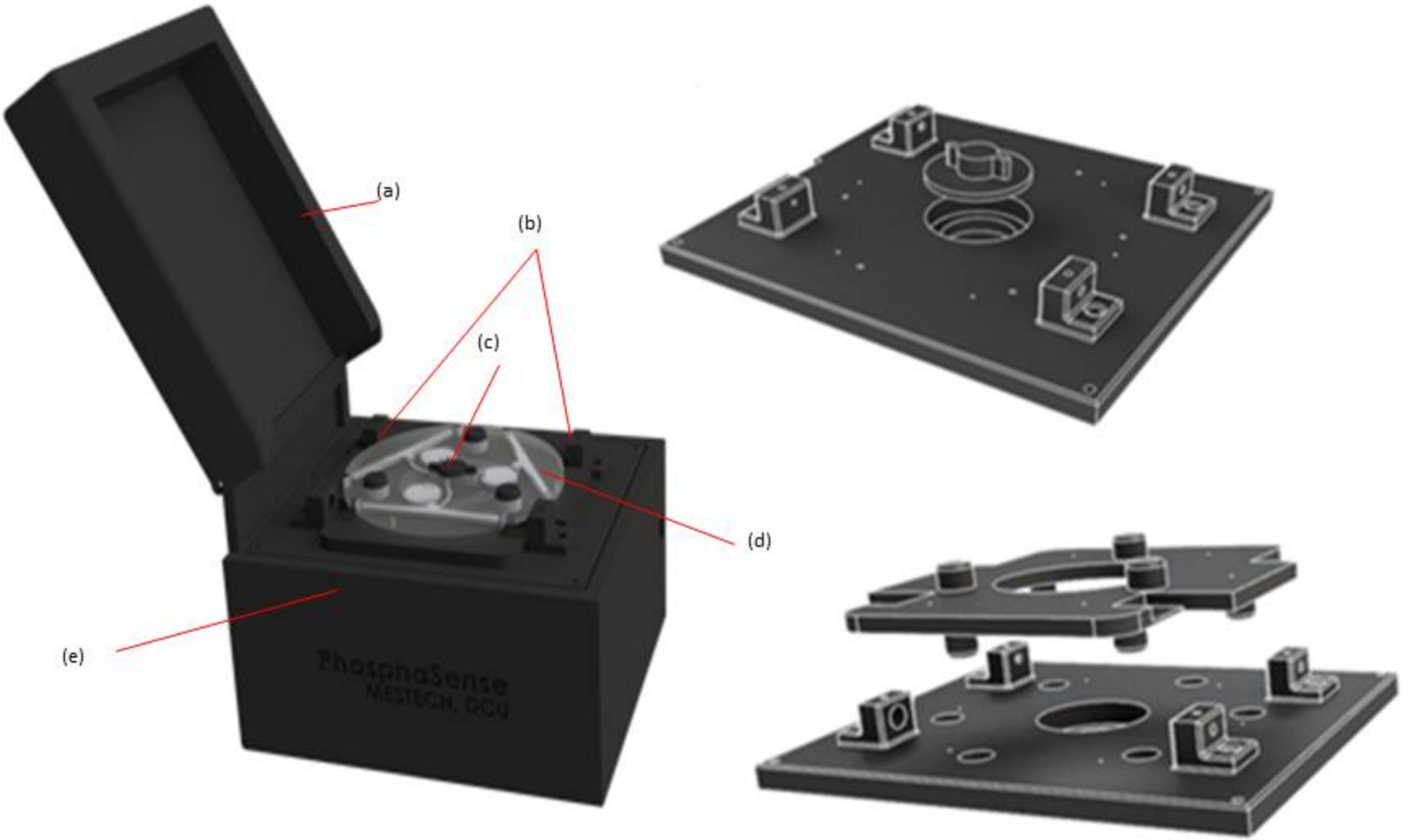
Table 4. The LOD, saturation point and sensitivity for the LED and laser at different optical path lengths.

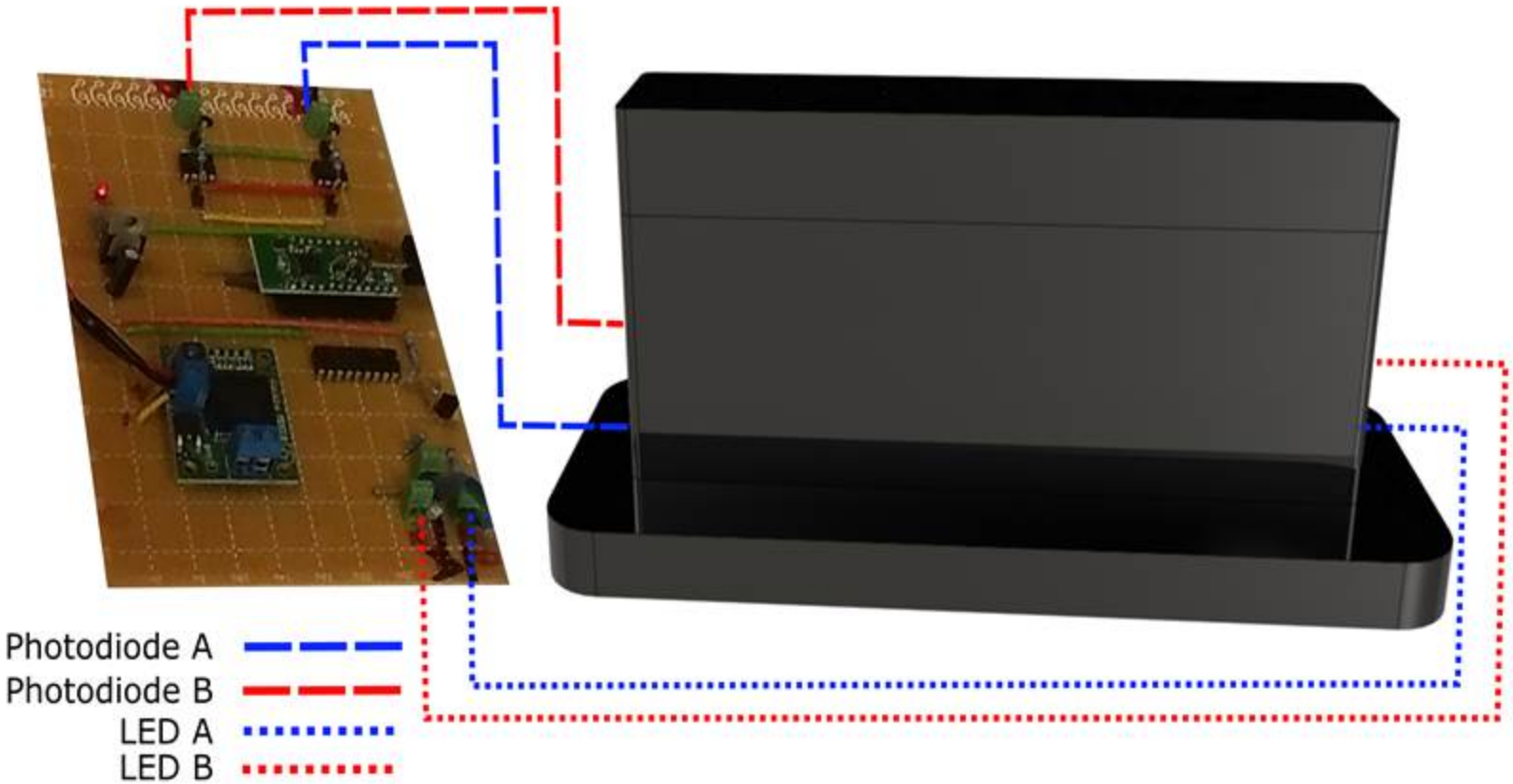
Path length (mm)	LOD ($\mu g.L^{-1}$)	Saturation point ($\mu g.L^{-1}$)	Sensitivity ($AU.L.\mu g^{-1}$)
LED			
2	231.39	N/A	-0.00004
5	121.25	N/A	0.0004
10	49.63	N/A	0.0006
50	77.07	800	0.003
100	1.23	400	0.0063
Laser			
2	461.97	N/A	0.00007
5	25.48	N/A	0.0003
10	24.69	N/A	0.0007
50	84.37	800	0.0022
100	32.22	400	0.006

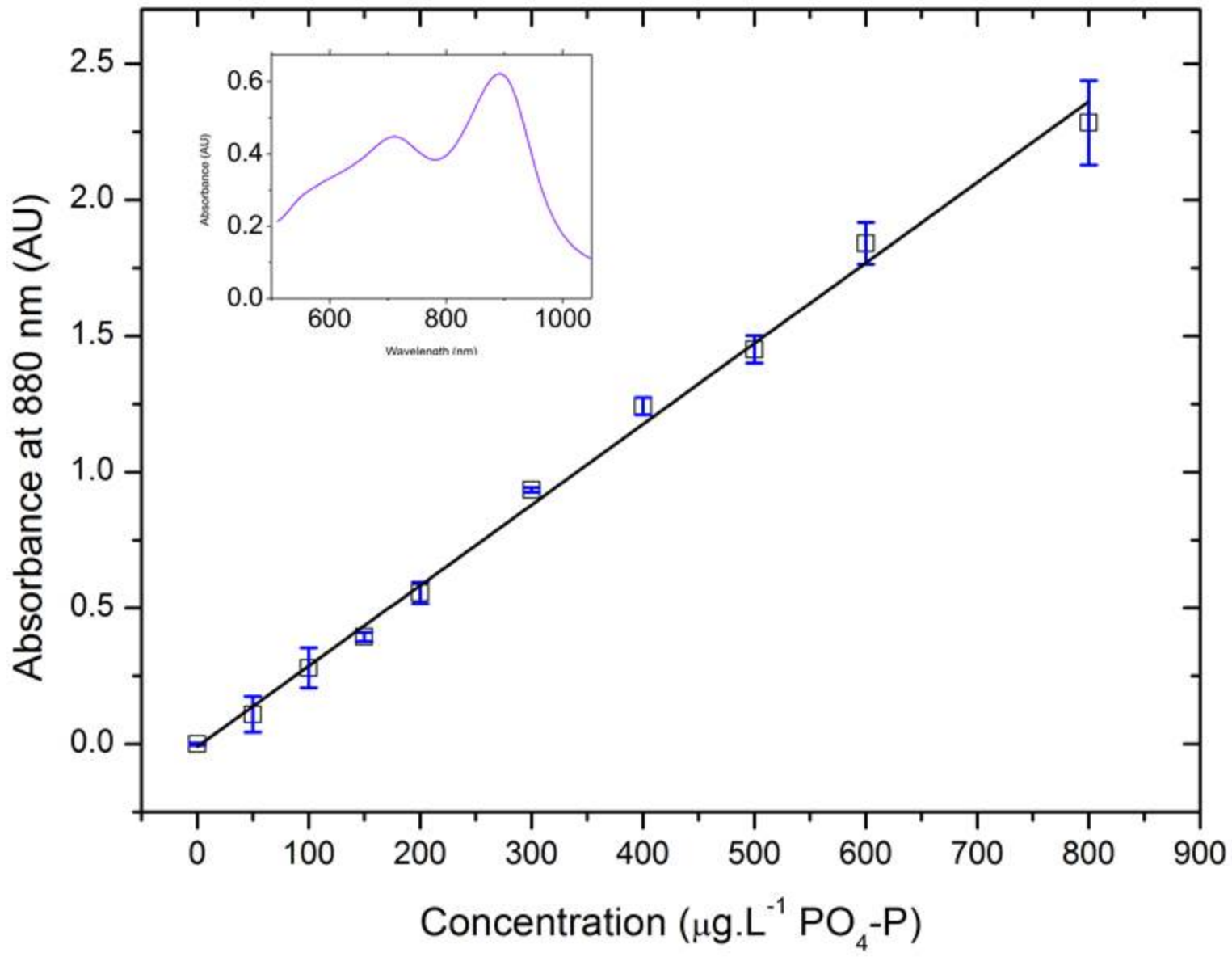

(i)
(ii)
(iii)
(iv)
(v)

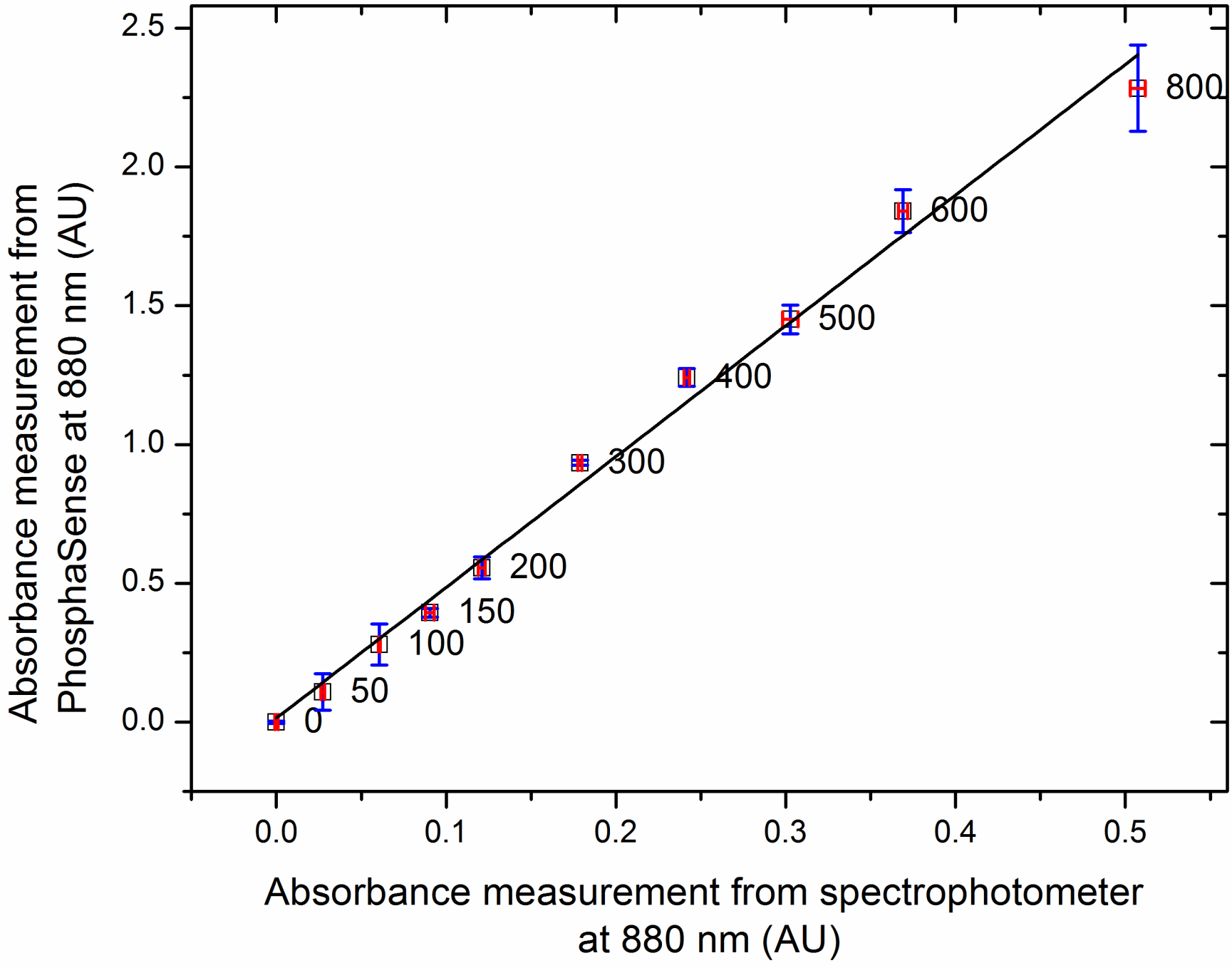

5.90mm


R
V
ODZ
75mm


(a)
(b)
(c)
(d)
(e)
PhosphaSense
MESTECH, DCU


Photodiode A
Photodiode B
LED A
LED B


Absorbance at 880 nm (AU)
Concentration (μg.L-1 PO4-P)
0.0
0.5
1.0
1.5
2.0
2.5
0
100
200
300
400
500
600
700
800
900
Absorbance (AU)
Wavelength (nm)
0.0
0.2
0.4
0.6
600
800
1000


Absorbance measurement from PhosphaSense at 880 nm (AU)
Absorbance measurement from spectrophotometer at 880 nm (AU)
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0
50
100
150
200
300
400
500
600
800