

Nutrient Monitoring in Marine Environments

Margaret McCaul, John Cleary, Eoghan McNamara and Dermot Diamond

Introduction

Nutrients such as phosphate, ammonia, nitrite and nitrate are central in many environmental processes within the marine environment, including several microbial, plant and animal metabolic processes. This work is carried out as part of the COMMON SENSE FP7 project. The COMMON SENSE project aims to provide a cost effective reliable sensing platform for in-situ measurements of key parameters relating to eutrophication, contaminants, marine litter and underwater noise. The project will design and develop new generation sensors focused on the detection of: Nutrient analytes by utilising established colorimetric chemistries for phosphate, ammonia, nitrate and nitrite, low concentrations of heavy metals (Pb, Hg, Cd, Zn and Cu), surface concentration of micro plastics, and underwater noise. The COMMON SENSE nutrient sensor will be based on a similar approach to the systems previously developed at DCU for autonomous detection of phosphate¹ and other parameters based on a combination of microfluidic analytical systems, colorimetric reagent chemistry, low-cost LED-based optical detection and wireless communications. Here we focus on the development of an autonomous sensor for the in-situ detection of nutrients by utilising colorimetric chemistries nitrite and nitrate.

Colorimetric Chemistries

The use of vanadium (III) Chloride has been proposed recently as a suitable alternative to cadmium column for the reduction of NO_3^- to NO_2^- in marine water^{2,3}. The use of VCl_3 as a reduction agent has advantages over the traditional Cd column method as it is less toxic than cadmium and does not require preparation of Cd coils or columns, is low cost and can provide fast analysis of a large series of samples at low volumes³. For Nitrite, 1 ml of sample/ standard solution was transferred to 1.5 ml Eppendorf vials, 50 μl of Griess reagent was then added to these vials and the resulting solution incubated at ambient temperature (approx. 23°C) for 20 minutes. For the direct determination of Nitrate, 100 μl of VCl_3 was added to 900 μl of sample/ calibration solution. Samples were incubated at 60°C for 20 minutes. All solutions were measured on a PerkinElmer UV-VIS-NIR Spectrometer L900 using a wavelength of 540 nm.

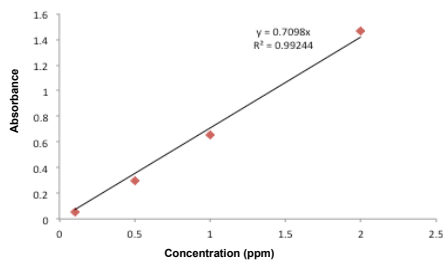


Fig. 1. Linear response for nitrite analysis in artificial sea water. Reactions were carried out at ambient temperature (approximately 25°C) for 20 min using 1 ml NO_2^- standards and 50 μl Griess-Reagent. This experiment was carried out in triplicate however the error bars in this graph are two small to be seen.

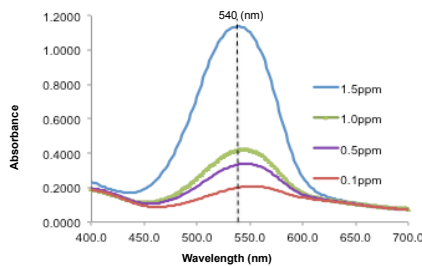


Fig. 2. Wavelength scan from 400 nm to 700 nm for low level nitrate standards. Maximum absorbance was observed at 540 nm, with a linear range from 0.05 ppm to 1.5 ppm.

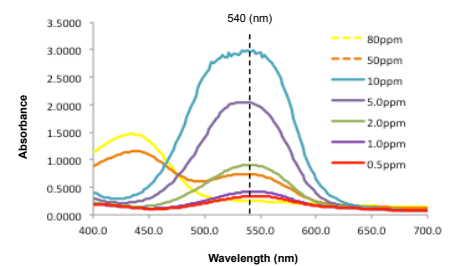


Fig. 3. Wavelength scan from 400 nm to 700 nm for high level nitrate standards. Maximum absorbance was observed at 540 nm, with a linear range from 0.5 ppm to 10 ppm. Despite a slight shift in lambda max, a significant response is retained above 10 ppm which could enable the dynamic range to be extended to higher concentrations.

Pre-competitive prototype design

A novel bench top system was developed in-house to systematically evaluate the Light emitting diodes (LED's) and Photodiodes (PD's). The system determines the current draw and voltage of both the LED's and PD's. In addition the modular design of the system allows for testing of each individual component to ensure that optimal operating conditions for each component is obtained prior to integration into the deployable system.

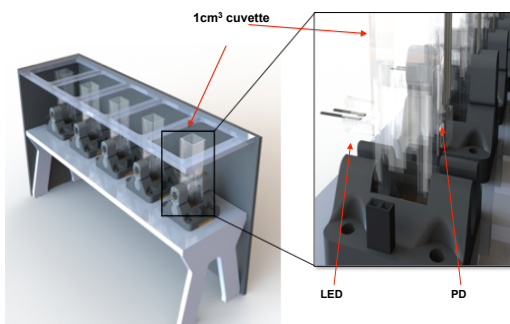


Fig. 4. A rendered image of the in-house developed bench top system. The front and side have been removed to show internal details. The LED's and PD's are mounted on slides allowing for them to be quickly and easily swapped out. This set up allows for measurements from up to 5 LED's and PD's to be taken under static flow conditions.

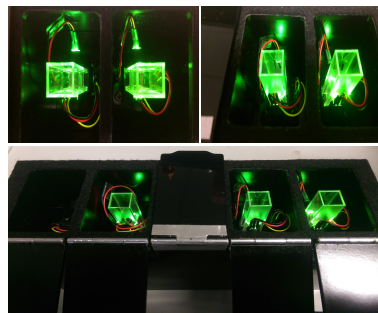


Fig. 5. Photographs of the physical bench top system in operation. The images here show 545 nm LED's passing light through a 1 cm³ cuvette containing nitrite standard solutions.

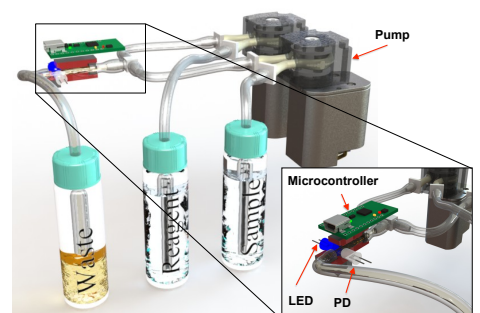


Fig. 6. A rendered image of the concept behind the dynamic flow measurement set up. This dynamic measurement will be performed in a microfluidic chip housed in the system shown in Fig. 4.

Acknowledgements

The authors would like to acknowledge funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under Grant Agreement No 614155, and from Science Foundation Ireland under Grant SFI/12/RC/2289 (Insight Centre for Data Analytics)

References

- Cleary, J., Maher, D., and Diamond, D. Development and deployment of a microfluidic platform for water quality monitoring. In: Mukhopadhyay, Subhas C. and Mason, Alex, (eds.) Smart Sensors for Real-Time Water Quality Monitoring. Smart Sensors, Measurement and Instrumentation. Springer-Verlag, Berlin Heidelberg 2013, pp. 125-148.
- García-Robledo E, Corzo A, Papaspyrou S. A fast and direct spectrophotometric method for the sequential determination of nitrate and nitrite at low concentrations in small volumes. Mar Chem 2014;162:30-6.
- Schneiger B, Lehners C. Determination of nitrate plus nitrite in small volume marine water samples using vanadium(III)chloride as a reduction agent. Mar Chem 2014 3/20:160-91-8.