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Ionogel-based Nitrite and Nitrate Sensor for Water Control at the Point-of-Need

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Abstract

The increment of uncontrolled nutrients concentration in water is the subject of increasing environmental concern. In particular, the increment of nitrate causes the eutrophication of algae, leading to fauna and flora demise.[1] In order to favour an easy and adequate monitoring of this environmental problem, we have developed an ionogel-based sensor for the colorimetric determination and image analysis detection of nitrite and nitrate in water. The sensor consists on a small poly(methyl)methacrilate (PMMA) device cut by a CO_2 laser where both the detection and the calibration zones are integrated. A simple photograph of the whole device, followed by colour processing of the different sections of the chip was used for the determination of nitrite concentrations.

Keywords: Nitrite Nitrate Sensor, Griess reagent, Ionogel, chip, paper-based analytical device

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1. Introduction

Over the past few years, great environmental monitoring developments have appeared in response to increasing contamination of natural, industrial and municipal water by toxicants and water pollutants such as harmful chemical agents. The determination of nutrients concentration in water is very important because these nutrients directly affect to water life equilibrium. As an example, eutrophication of algae due to the increment of nitrate causes detrimental human health and marine life degradation. [1]

The colorimetric determination of nitrite by Griess reagent is chemically robust, offers excellent analytical performance and has been applied in the development of several analytical platforms. [2] However, these systems are usually complicated devices consisting of reagents reservoirs, pumps, valves and detector modules, making the final platform expensive and not adequate for on-site use.

Protocols from environmental monitoring agencies normally involve manual sampling on-site, followed by transportation to an equipped facility where the analysis is carried out by highly trained personnel using sophisticated instrumentation. This strategy obtains very precise and accurate results, and properly adjusts to regulatory legal proceedings. In contrast, expenses associated with maintaining these facilities, instrumentation and personnel lead to elevated costs and so diminish the amount of samples analysed over time. The use of microfluidic technology is emerging as an alternative capable of approaching water monitoring to society. Microfluidics generates easy manageable and affordable equipment that can be used at the point of need. [3]

Stimulus responsive materials, known as "smart materials", have gained increasingly high attention due to their autonomous behaviour in response to changes in their local environment. For instance, these smart materials have been integrated as valves into microfluidic platforms for improving autonomous performance during analysis.[4] In particular, ionogels, polymer gels that incorporate ionic liquids (IL) in its polymer matrix, are cheap alternative materials that can be used as reagent storage [5] and sensors [6], showing low reagents consumption and easy operability.

This study demonstrates the colorimetric detection and subsequent determination of nitrite and nitrate concentrations in water samples by using ionogel-based sensors that incorporate the Griess reagent in their polymer matrix. The ionogels were *in situ* polymerised into the microfluidic devices containing five calibration points and a sensor area for nitrite analysis. The detection of nitrate is carried out by injecting the sample in the reservoir, then the sample is forced to pass through a reduction area fabricated in a paper-based microfluidic device, where all nitrate is reduced to nitrite. Finally, the Griess reaction takes place in the sensor area and the nitrite concentration is determined by its colour change.

2. Methodology

The sensor was fabricated in PMMA cut by a CO_2 laser. The sensor was designed with five calibration reservoir points and an additional "key-shape" reservoir for the sample. The ionogel was synthesised following the protocol described previously by us. [7] Briefly, the ionogel was synthesised using *N*-isopropylacrylamide, *N,N'*-methylene-bis(acrylamide) and a photoinitiator (2,2-dimethoxy-2-phenylacetophenone) dissolved in 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid, by mixing and heating at 80 °C for 30 min. The chemical structure of the ionogel components is illustrated in Figure 1.
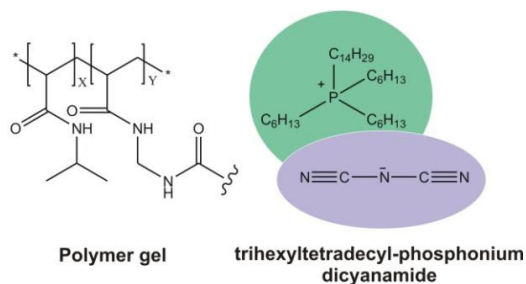
Figure 1: Chemical structure of the components of the ionogel. Left: polymer gel based on N-isopropylacrylamide and N,N`-methylene-bis(acrylamide); right: trihexyltetradecyl-phosphonium dicyamide IL.

5 µL of the mixture were spiked into each reservoir and UV photopolymerised for 20 min. The nitrate of the sample can be easily reduced to nitrite with metallic Zn which oxidises to Zn (II). An emulsion of metallic Zn in ultrapure water was deposited within the paper channel and placed in the "key-shape" as shown in Figure 2. Then, the ionogels were embedded with the Griess reagent three times and left to dry for 12 hours.
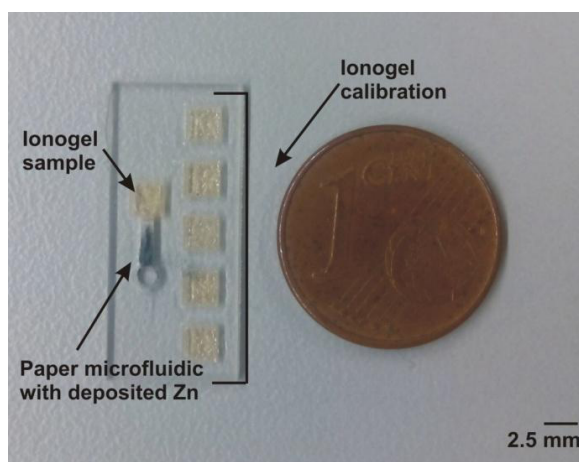

Figure 2: Picture of the ionogel-based nitrate and nitrite sensor. The sensor consists of five calibration ionogels sections and a sensor area connected to a paper-based microfluidic device with deposited metallic Zn.

3. Results

As a proof of principle, nitrite calibration solutions were prepared in the lineal range of 0 - 10 ppm and 3 µL of each solution were added to the five calibration points. After 30 min, different shades of orange developed for each nitrite concentration. The nitrate sample was added to the Zn reduction area which moved towards the ionogel sensor area by the paper capillarity forces, revealing the final orange colour. Pictures of the colored ionogels were taken with a Nikon camera and processed by image analysis. Luminance (L), chromaticity (C) and hue (H) parameters were taken in PhotoShop CC by pixelling each ionogel and the nitrate sample's concentration calculated using a multivariate calibration model, Figure 3. Results showed a concentration of 5.0 ± 0.5 ppm which agrees well with the spiked solution of 5 ppm.

4. Conclusions

This novel nitrite and nitrate sensor methodology, which will be soon transferred to a smartphone detector with an image analysis application, could help in the detection of both nitrite and nitrate concentrations at the point-of-need, since it is a cheap, portable, and reagent manipulation free device.
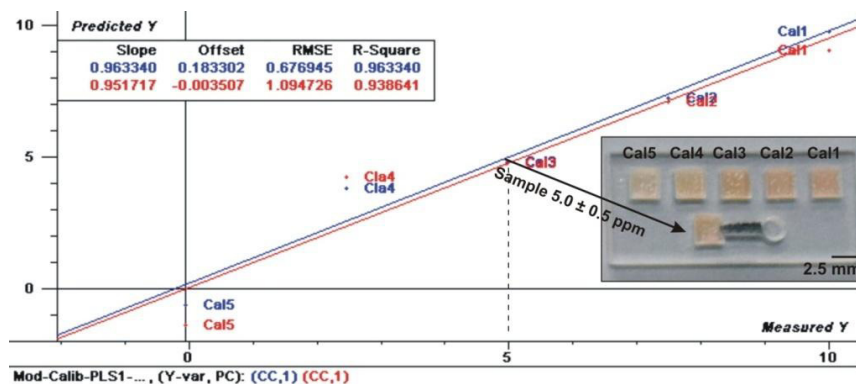

Figure 3: Multivariate calibration model (blue) and validation (red) curves generated after image analysis for Cal5 (0 ppm), Cal4 (2.5 ppm) Cal3 (5 ppm), Cal2 (7.5 ppm) and Cal1 (10 ppm). Inside, an ionogel-based nitrite and nitrate sensor picture showing the change of colour for each calibration point and for the sample.

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