CL:AIRE INSPIRATION bulletin

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CL:AIRE's INSPIRATION bulletins describe practical aspects of research which have direct application to the management of contaminated soil or groundwater in an agricultural context. This bulletin describes different optical and electrochemical methods for achieving real-time monitoring of nitrate in water.

Development of sensors for monitoring nitrate in groundwater

1. Introduction

Monitoring the quality of our water resources is important to identify sources of contaminants, determine environmental hazards to human health and assess the effectiveness of clean-up or management measures. To ensure the protection of the subsurface, the EU Water Framework Directive prohibits direct discharges of pollutants to groundwater and requires the Member States to monitor their groundwater bodies. Nitrate is a common pollutant of freshwater and groundwater, with the agricultural sector being an important source. The intensification of European agriculture, which began in the early 1940s, has resulted in increased inputs of nitrogen (N) and phosphorus (P) in soils, due to the extensive use of fertilisers and manure. In turn, this has increased runoff of N and P to water bodies, resulting in problems with eutrophication and leaching of nitrate to groundwater (Kros *et al.*, 2015). Although the effects of increased nitrate levels on human health are unclear due to the limited number of well-designed studies (Ward *et al.*, 2018), nitrate contamination of the subsurface still constitutes a concern due to its environmental impacts. These negative effects can be minimised and, in many cases, prevented by the implementation of efficient monitoring strategies for which accurate information on nutrients' concentration and fluxes is essential. Currently, there are two main types of nitrate sensors for real-time monitoring: electrochemical (Ion Selective Electrodes, ISE) and optical sensors. The continuous monitoring of nitrate concentration over extended periods of time is usually performed with optical nitrate sensors, which rely on the direct transmission and absorption of ultra violet (UV) light by nitrate. Optical UV sensors are usually preferred over the traditional electrochemical sensors, due to their higher precision, lower drift and less frequent calibration. However, the performance of these sensors can be influenced by environmental conditions, such as in the presence of saline water (Huebsch *et al.*, 2015). The research presented here aims to identify different techniques and materials for achieving real-time monitoring of nitrate in water. For this purpose, both optical and electrochemical methods are examined and presented in the following sections.

2. Optical Sensing Using Ionophores

The main optical sensing mechanism examined for nitrate sensing in this study is based on the combination of a nitrate ionophore and a chromoionophore (pH indicator) incorporated into a suitable matrix. The former is responsible for the bonding with the targeted ions (nitrate) and the latter with hydrogen ions in water. When the membrane containing the above components is introduced into a nitrate-enriched aqueous medium, a co-extraction of nitrate and hydrogen ions to the membrane occurs. The co-extraction should take place in a buffered environment, to ensure that the concentration of hydrogen ions remains stable. This process induces the protonation or deprotonation of the chromoionophore resulting in changes in absorbance, which are monitored with respect to the activity of nitrate ions in water, using a UV-Vis spectrophotometer. The changes in absorbance occur in the visible spectrum due to the presence of the chromoionophores. These compounds provide an indirect monitoring of nitrate activity in a sample, where higher absorbance values during protonation indicate higher nitrate activity and, respectively, lower absorbance indicates lower activity. When the sensing membrane is immersed into the nitrate-enriched water, an equilibrium is established between the aqueous phase and the membrane, as shown below, where I and C represent the ionophore and chromoionophore respectively:

$$\mathbf{H^+_{(aq)} + NO^-_{3\,(aq)} + C_{(org)} + I_{(org)} \rightleftharpoons INO^-_{3\,(org)} + CH^+_{(org)}}$$

Considering the mass and charge balances that govern the above equilibrium, the response function of the sensing mechanism can be described by the following equation:

$$\alpha_{H^+}\,\alpha_{NO_3^-} = \frac{1}{K_{coex}}\,\frac{(1-\alpha)^2}{\alpha}\,\frac{C_T}{I_T-(1-\alpha)\,C_T} \qquad \text{Equation 1}$$

where
α_{H^+} is the proton activity (instead of concentration),
$\alpha_{NO_3^-}$ is the nitrate activity,
K_{coex} is the co-extraction constant,
C_T is the total concentration of chromoionophore, and
I_T is the total concentration of ionophore.

The term α denotes the deprotonation degree of the chromoionophore, or else, the fraction of the deprotonated chromoionophore concentration to the total chromoionophore concentration. The response function of the membrane can be plotted using the deprotonation (or protonation) degree and the nitrate ion activity from experimental data, a process which can also result in the estimation of the co-extraction constant. In this study, two different types of nitrate ionophores were examined using this sensing mechanism; a tetra-azacycloeicosane compound (nitrate

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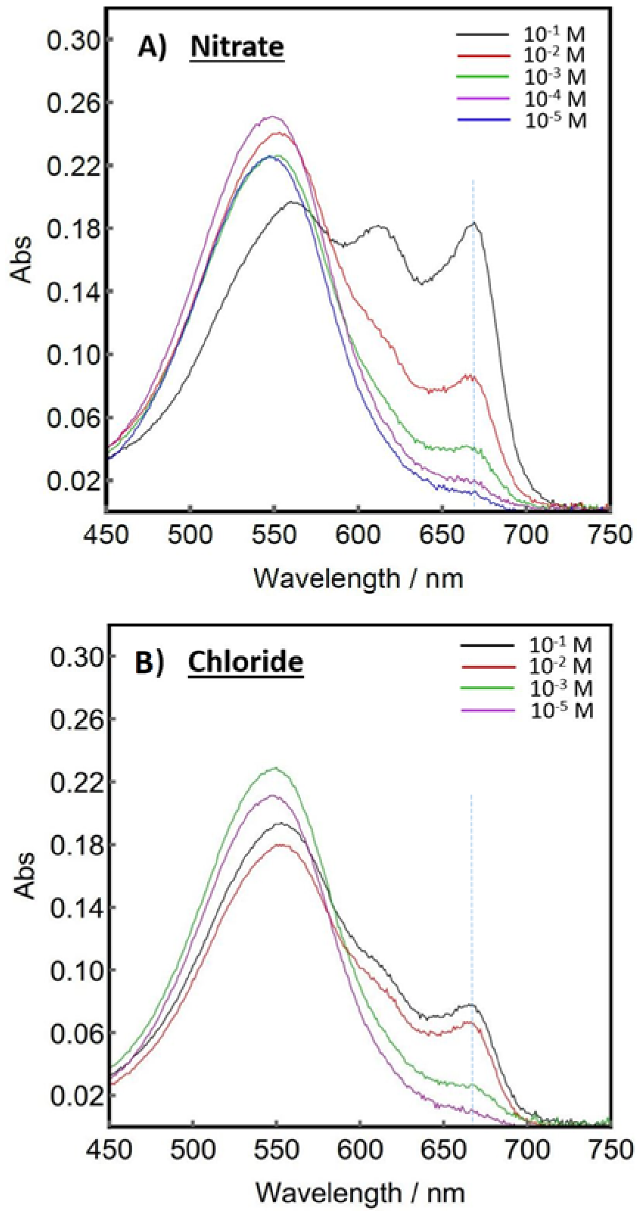

Figure 1. Membrane absorbance spectra after immersion in A) nitrate and B) chloride solutions.

ionophore VI) and a bis-thiourea compound (nitrate ionophore V). The chromoionophore chosen for this study had a protonation peak at 663 nm. Sensing membranes were prepared based on the abovementioned compounds, and changes in their absorbance after the immersion of the membranes in nitrate solutions were recorded.

Testing both nitrate ionophores in membranes of identical compositions showed that, although the sensors were nitrate-sensitive, eventually, both ionophores were prone to chloride interference. As shown in Figure 1, the membranes are responding to the increase of nitrate concentration by an increase of the protonation peak of the chromoionophore at 663 nm. A similar pattern is observed for chloride as well, proving that chloride can act as an interfering ion for the sensing membrane. This is particularly important because chloride is often present in groundwater at concentrations that can reach up to 1 mM, as happened in the case of Wallonia, Belgium (SPW, 2019).

3. Electrochemical Sensing Based on Potentiometry

The Ion Selective Electrodes (ISEs) are potentiometric sensors that typically work under zero current conditions in a setup consisting of two electrodes; the indicator electrode and the reference electrode, which represent the cathode and anode of the system, accordingly. The measured potential difference between the cathode and the anode is the sum of all potential differences in the system. For the proper function of an ISE, all the potentials should be independent of the sample composition, apart from the potential at the interface between the sample and the membrane. Ideally, the potential change (E_I)at the ion selective membrane (which is permselective to the primary ion and attached to the indicator electrode) is proportional to the change of the logarithmic ion activity and described by the Nernst equation, which, at room temperature (298 K), is simplified in the following form:

$$E_I = K_I + \frac{s}{z_I}\log\alpha_I \qquad \text{Equation 2}$$

where, K_I is an experimentally determined constant potential value, s is the Nernstian slope of 59.18 mV divided by the charge z_I of the primary ion and α_I the activity of the primary ion.

There are two distinctive categories in ISEs: the inner-solution electrodes and the solid-contact electrodes. The former represent the conventional polymer-based ISEs, where the ion selective membrane separates the sample from an internal electrolyte solution. For nitrate, this is usually a mixed solution of a chloride and nitrate salt, e.g. sodium chloride and sodium nitrate. This internal electrolyte solution has a double function; the constant chloride activity can provide a constant potential at the interface between the electrolyte and the chlorinated silver wire (typical material used for electrodes) and the constant nitrate activity provides a constant phase-boundary potential at the interface between the electrolyte and the ion selective membrane. With this configuration, long-term stable potentials and reproducible responses of the electrodes can be achieved. However, this setup cannot be easily miniaturised, which precludes its use in many small-scale applications and its potential cost reduction in the case of mass production. Solid-contact ion selective electrodes (sc-ISEs) overcome these limitations. Their difference lies in the replacement of the internal electrolyte and the internal electrode by a solid ion-to-electron transducer and an electronically conductive substrate, respectively. Advantages of this setup, apart from the possibility of miniaturisation, is maintenance-free operation and the fact that they can be used at any orientation as well as at elevated temperature and pressure. Over the last decades, much attention has been given to the examination of suitable materials for use as solid ion-to-electron transducers. Currently, the most promising ones include several conducting polymers and different carbon nanostructures (Bieg *et al.*, 2017). Examples of different nanostructured materials that have been used as transducers in solid-contact electrodes include three-dimensionally ordered macroporous carbon (Lai *et al.*, 2007), carbon nanotubes (Crespo *et al.*, 2008) and graphene (Hernandez *et al.*, 2012). The purpose of these materials is to convert effectively the ionic signal to electronic signal from the ion-selective membrane to the transducer. Carbon nanotubes are highly hydrophobic, do not involve redox reactions and are insensitive to light. These characteristics give them an advantage over the electroactive polymers that are commonly used today as transducers (Crespo *et al.*, 2009). A more recent study

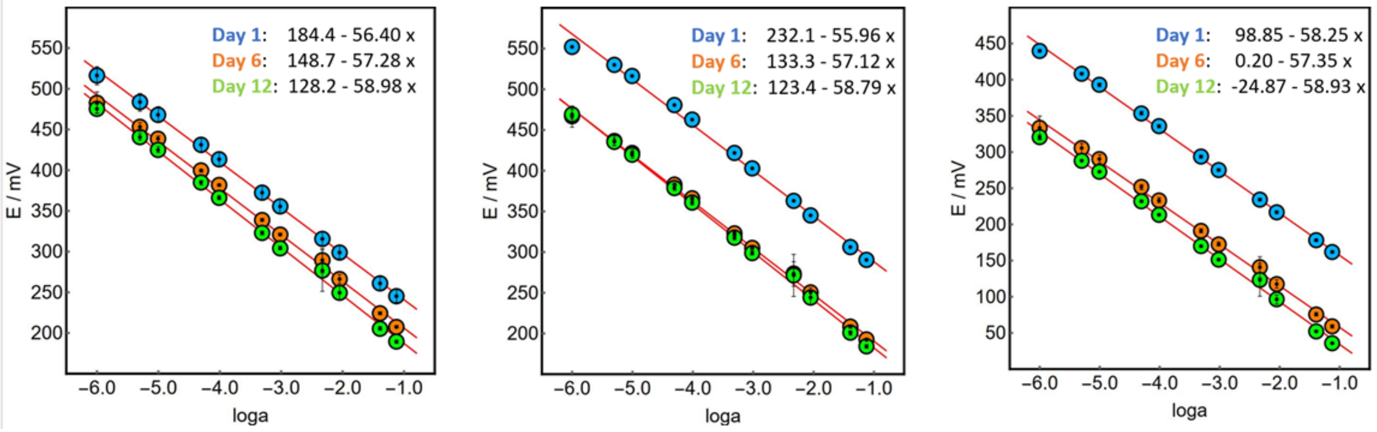

Figure 2: Calibration curves for nitrate sensing in PVC:DEHP (left), PVC:NPDE (centre), PU:NPDE (right) membranes. "loga" refers to the logarithmic activity of nitrate ions.

where functionalised carbon nanotubes were used for anion detection in environmental samples was performed by Yuan *et al.* (2015), which formed the basis for the work presented here.

The purpose of the present study is the nitrate detection using those functionalised lipophilic carbon nanotubes by testing different membrane combinations. The ion-selective membrane examined here contains 10 mmol/kg of ion exchanger TDMAN (tridodecylmethylammonium nitrate) which replaced the ionophore used in the previous experiment, and 15 mmol/kg of a lipophilic salt (ETH 500) used to decrease the resistance and minimise the ion-exchange of hydrophilic ions in the membrane. For the preparation of the plasticised membrane, different polymers (polyvinyl chloride, PVC and polyurethane, PU) and plasticisers (DEHP and NPDE) were tested in the following ratios: 1:2 for PVC:plasticiser and 1:1 for PU:plasticiser. The calibration curves for three different membranes with the same concentration of ion exchanger and lipophilic salt are presented in Figure 2.

In all cases, the detection limit for nitrate ions is 10^{-6} M, which is considerably lower than the concentration observed in groundwater (SPW, 2019). The slopes of the response curves are close to Nernstian, with only a slight decrease over 12 days. All three types of sensors show a gradual loss of stability over time, while the PVC:DEHP membrane showed the least decrease of K_I value for the whole period. In order to examine the influence of chloride, which was the main interference encountered earlier, the same type of experiments were performed, under NaCl background ranging from zero to 0.6 M chloride (seawater). For comparison purposes, an inner -liquid ISE was used. As can be seen in Figure 3, the presence of 1 mM chloride increases the detection limit of the sensor to 10^{-5} M nitrate, which is not considered limiting in the case of groundwater and freshwater. At these chloride levels, the slope of the response curve stays close to Nernstian (54.01 mV/decade). However, when it comes to the seawater chloride background, the detection limit increases considerably and the sensor cannot be used for nitrate sensing. A decrease in K_I value is observed in the case of the solid-contact electrode over increasing chloride background, which should be the objective of further examination.

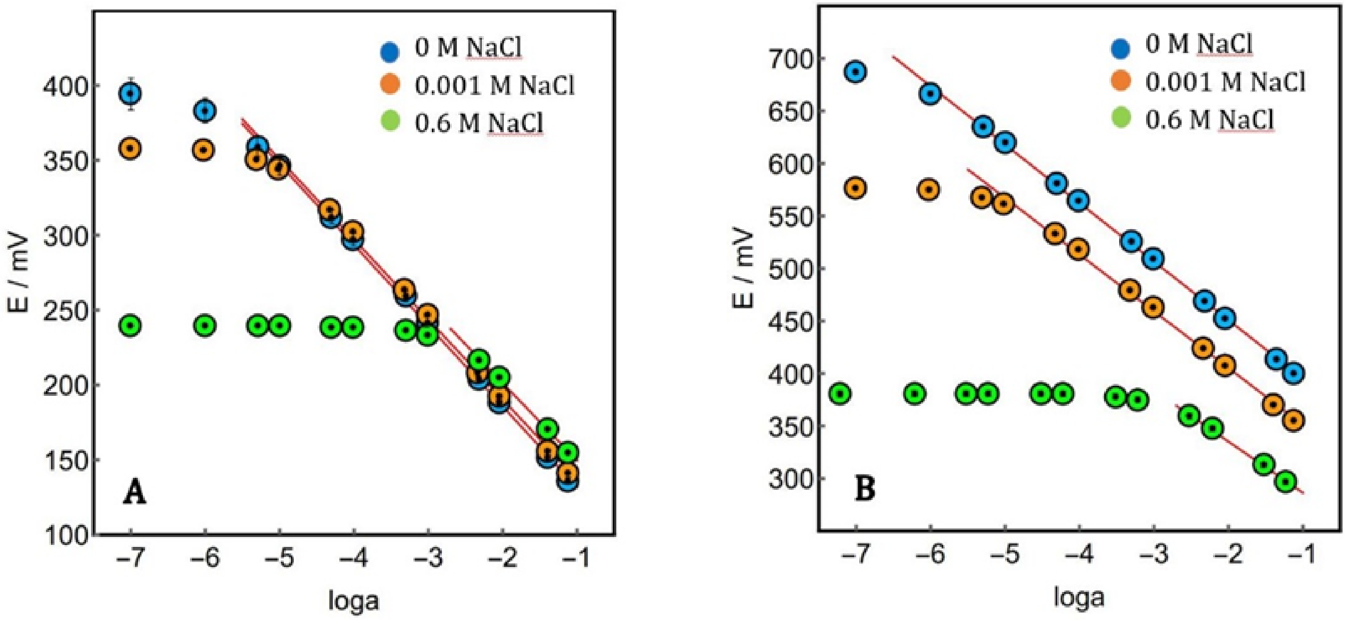

Figure 3. Calibration curves for nitrate with and without chloride background: A) Inner-solution ISE and B) fCNTs ISE. "loga" refers to the logarithmic activity of nitrate ions.

4. Conclusions

Two different methods for monitoring nitrate have been tested. The first method, an optical sensing mechanism based on the use of ionophores, presented a significant interference from chloride ions, precluding its further examination and optimisation. The second method, based on solid-contact ion selective electrodes with functionalised carbon nanotubes, presents a decreased interference from chloride and detection limits up to 10^{-5} M nitrate. The results from this research are promising; however, further optimisation of the method is needed to increase the stability of the sensors.

Acknowledgments

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