Secondment report

January 1st – June 30th 2019

University of Geneva

Project title: Development of sensors for monitoring nitrate in groundwater

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ESR 2 – Work Package 1

UNIVERSITÉ DE GENÈVE
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This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675120.

Abbreviations

ACN	Acetonitrile
DEHP	Dioctyl phtalate
ETH 500	Tetradodecylmethylammonium tetrakis (4-chlorophenyl) borate
GC	Glassy carbon
CNT	Carbon nanotube
ISE	Ion Selective Electrode
PEDOT	Poly(3,4-ethylenedioxythiophene)
TDMAN	Tridodecylmethylammonium chloride
THF	Tetrahydrofuran
UNIGE	University of Geneva

Contents

Secondment information

Host: University of Geneva (UNIGE)
Supervisor at the host organization: Prof. Eric Bakker
Duration: 01.01.2019 – 30.06.2019
Total length: 6 months

Motivation

The secondment took place at the Department of Inorganic and Analytical Chemistry of UNIGE. It started at the beginning of my third fellowship year. The expertise of the UNIGE group on electrochemical sensors and the progress of my research until the end of the 2nd year were the motivations behind my choice to perform this secondment at the specific research group.

Having as the main objective the monitoring of nitrate in groundwater, in the beginning of my fellowship (1st year) I started working with an optical method. This method comprised the use of ionophores, compounds that can selectively bind to specific ions. Since my emphasis was on nitrate ion, I focused on the examination of two nitrate ionophores. When these ionophores proved to be not as selective as needed (showing important interference from chloride ion), a new method needed to be found. Considering the existing difficulties behind the use of optical methods for real-time monitoring, my interest was then focused on the electrochemical sensing. Knowing the long-term experience of the UNIGE group on this field, I considered that this is the most appropriate place to perform my secondment.

Aim

The advances on the sector of electrochemical potentiometric sensors made the use of solid-contact ion selective electrodes (ISEs) feasible, moving away the traditional inner-solution electrodes. This change enables the minimization of the sensors and opens the road for many new applications. For the 6-month period of the secondment, the aim of my research was the development of solid-contact ISEs for monitoring nitrate and other ions of interest.

Description of experimental work & main results

In the following sections, the most important findings of the experimental work performed during my secondment are presented.

In order to gain some experience with the specific type of sensors, initially, the classical type of ISEs (inner-solution electrodes) was tested with nitrate solutions. The influence of the chloride was also examined by performing experiments in NaCl background. The membrane composition used for these experiments was: 10 mmol/kg TDMAN, 15 mmol/kg ETH500, PVC 33% w/w, DEHP 66% w/w. TDMAN is the ion exchanger that is responsible for nitrate sensing, ETH500 is a lipophilic salt that decreases the resistance and minimizes the ion-exchange of hydrophilic ions in the membrane, PVC is the polymer used as a membrane matrix material and DEHP the plasticizer. The following steps took place for the preparation of the inner-solution ISEs: i) dissolution of membrane components in THF, ii) drop casting (Ø 22mm) in glass plate, iii) overnight drying in ambient T, iv) cutting of membranes (Ø 8mm) & mounting on the electrode body, v) overnight conditioning in 10^{-3} M $NaNO_3$. The experiments were performed with three concentrations of chloride as background: 0M, 10^{-3}M and 0.6M NaCl. The later represents the seawater level of chloride.

After the preparation and testing of the inner-solution electrodes, solid-contact ISEs with the same membrane composition were prepared and tested similarly in chloride background. In this type of ISEs, the inner-solution is replaced by the transducer, which in our case was a layer of functionalized multi-walled carbon nanotubes. The preparation steps were: i) polishing of the glassy electrodes (Ø 3mm), ii) drop casting of the carbon nanotubes solution (1mg/mL), iii) dissolution of membrane components in THF, iv) drop casting of membrane solution, v) 1 hour drying in ambient T and vi) overnight conditioning in 10^{-4} M $NaNO_3$.

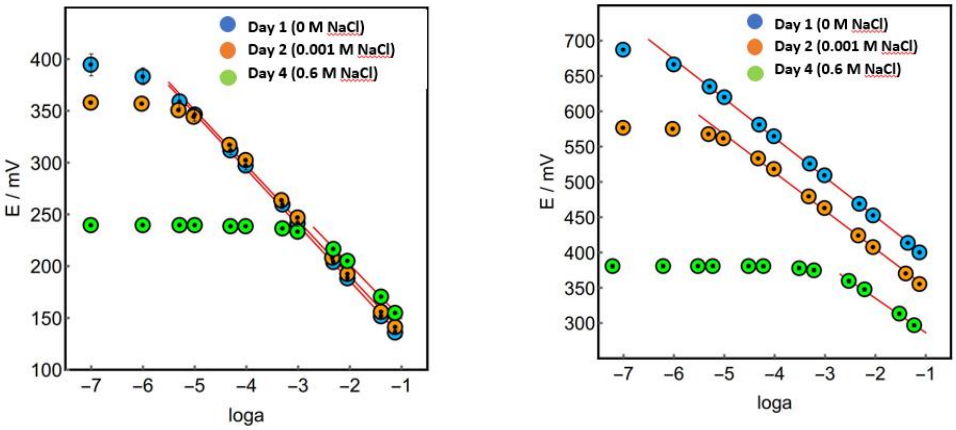


Figure 1: Calibration curves for nitrate with and without chloride background: Inner-solution electrodes (left) and solid-contact CNTs electrodes (right)

NaCl concentration	Inner-solution	Solid-contact (CNTs)
0 M	77.84 – 53.92x	339.5 – 55.69x
0.001 M	83.54 – 53.44x	297.2 – 54.01x
0.6 M	95.50 – 48.75x	237.7 – 48.72x

Table 1: Response curves for nitrate with and without chloride background

A different transducer, called PEDOT-C_{14}, was also tested for the solid-contact electrodes. It is a conductive polymer, which was electrochemically deposited on the electrodes. The following steps were performed for the preparation of the electrodes: i) polishing of the GC electrodes (Ø 3mm), ii) electropolymerisation with PEDOT-C_{14} (TPFPhB) solution, iii) manual rinsing with ACN, iv) overnight drying in ambient T, v) drop casting of membrane solution and vi) overnight conditioning in 10^{-4} M $NaNO_3$.

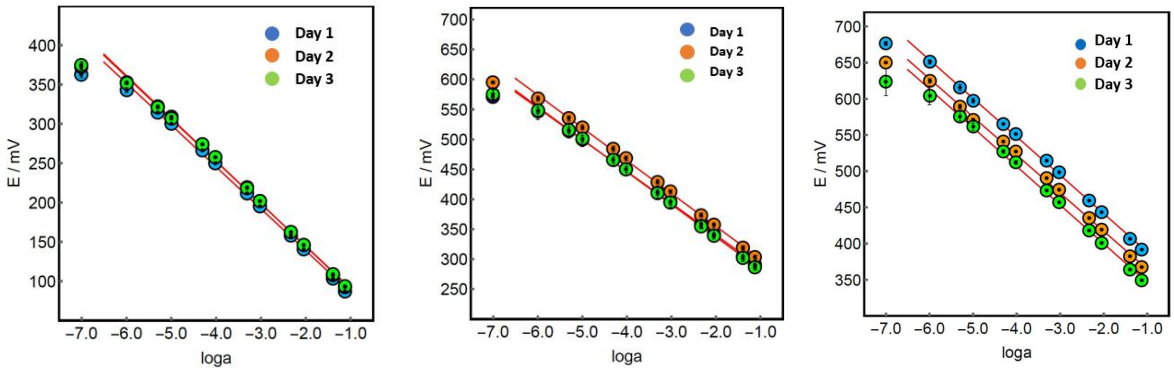


Figure 2: 3-day calibration curves for nitrate without background chloride concentration: Inner-solution electrodes (left), CNTs electrodes (middle), PEDOT-C_{14} electrodes (right)

	Inner-solution	Solid-contact (CNTs)	Solid-contact (PEDOT-C_{14})
Day 1	32.14 – 53.29x	233.9 – 53.11x	335.3 – 53.06x
Day 2	35.74 – 54.27x	245.1 – 54.83x	312.0 – 52.60x
Day 3	36.78 – 53.89x	228.4 – 54.33x	293.0 – 53.42x
Day 6	36.56 – 54.17x	193.5 – 54.45x	282.1 – 49.43x

figu 2: Response curves for nitrate without chloride background

For all the electrodes presented above, a 24h monitoring period in 10-4 M $NaNO_3$ (including the overnight conditioning) preceded the measurements to ensure that their signal is stable before the 3-day experiments. The results of this monitoring are presented in the following graph for all the electrodes.

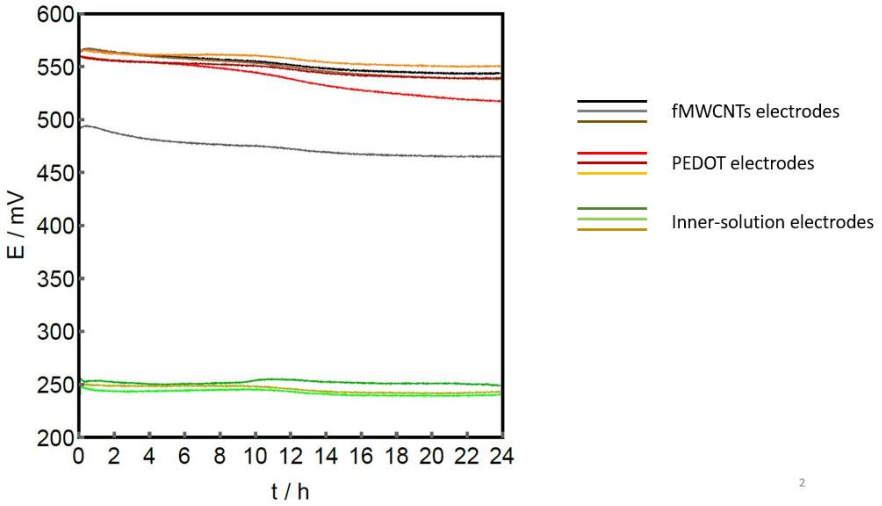


Figure 3: 24h response of the electrodes before the 3-day experiments

Moreover, the reproducibility of the electrodes was examined by alternating nitrate solutions of 10^{-3} M and 10^{-4} M. In all cases, the signal remained stable after several alterations, which proves that under the experimental conditions examined, the sensors signal is reproducible.

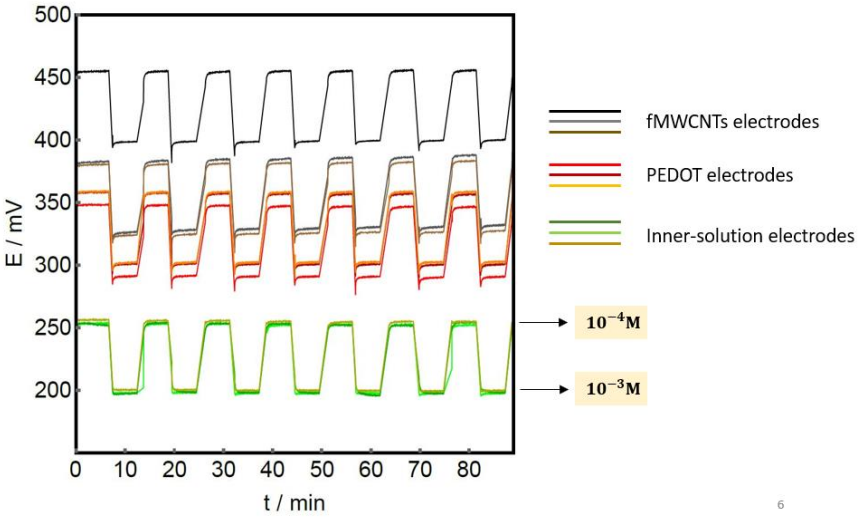


Figure 4: Reproducibility test for all electrodes

In the case of the solid-contact electrodes, a "water-layer test" was performed, in order to examine if there is water trapped between the electrode and the transducer that can interfere with the measurements.

The solid-contact electrodes shown above belong in the category of macroelectrodes, having a 3mm diameter of the glassy carbon rod. Since the miniaturization of the electrodes is possible with the solid-contact transducer, smaller-size electrodes (150μm Ø) were also tested. Initially, some pH measurements were performed, giving satisfactory results over a 6-day period. The transducer remained the same (CNTs) and the coating of both carbon nanotubes and membrane was performed by dipping the electrodes in the respective solutions. Two different types of membrane matrix were examined, with polyvinyl chloride (PVC) giving a higher detection limit than polyurethane (PU), as shown below. The stability of the electrodes was good for the first two days, but started showing some drift over the next period, as shown in Figure 5.

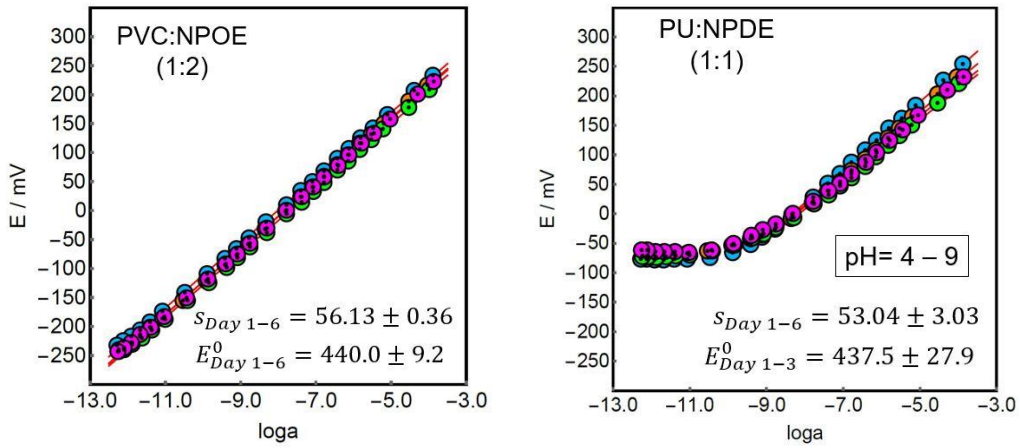


Figure 5: 6-day calibration curves for pH: PVC membrane (left), PU membrane (right)

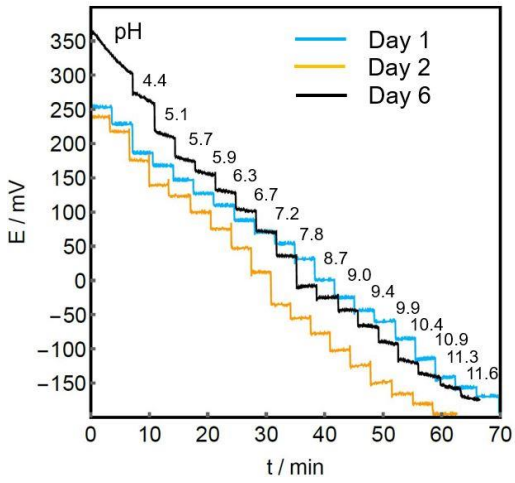


Figure 6: Potential vs time during pH calibration of a miniaturized electrode over a 6-day period

Following, nitrate measurements using the same membrane composition (as with the macroelectrodes) were performed. The results were not so satisfactory in this case, since both the stability of the electrodes and the detection limit worsened. Also, the response was sub-Nernstian, contrary to the Nernstian response achieved with the macroelectrodes.

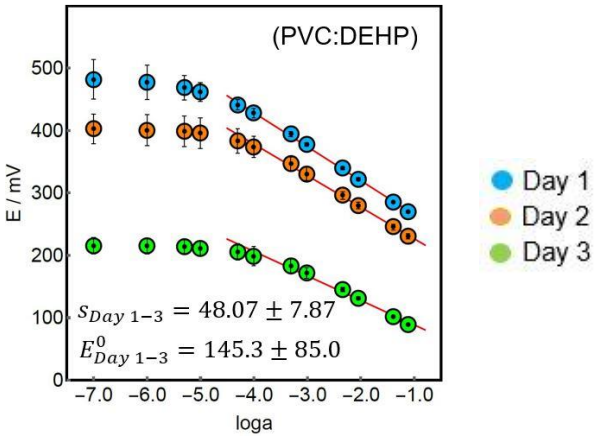
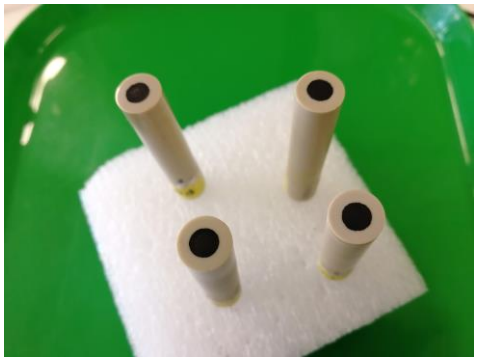


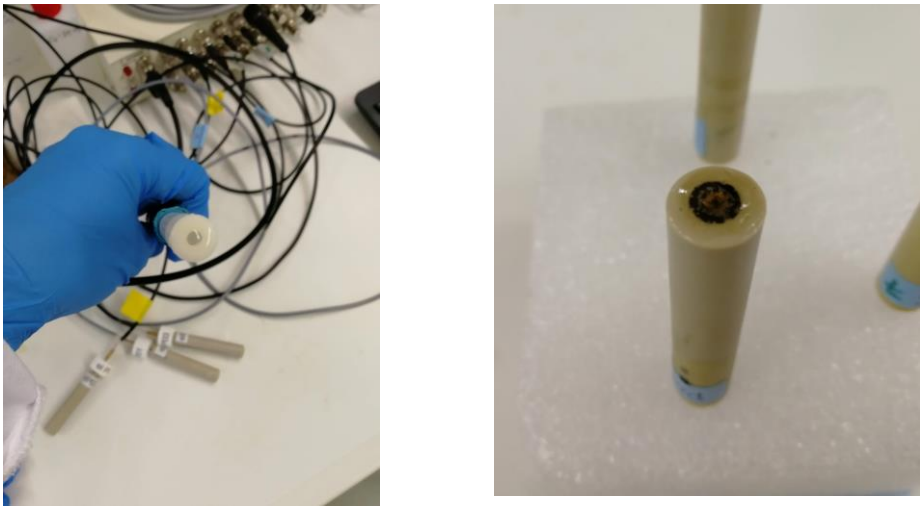
Figure 7: Nitrate calibration curves for the miniaturized electrodes

Overall, the solid-contact macroelectodes (3 mm Ø) seem to provide the most satisfactory performance for nitrate measurements so far. However, further optimization is needed to achieve better stability over time.

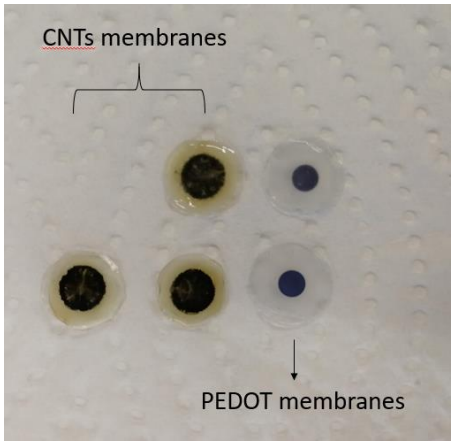
Photos



Solid-contact electrodes after carbon nanotubes deposition and before membrane deposition.



Inner-solution electrode (left) and solid-contact CNTs electrode (right)



CNTs and PEDOT plasticized PVC membranes