

## Detection of Nutrients and Species Relevant to the Carbon Cycle in Seawater Previously Desalinated and Acidified

### Motivation

The determination of nutrients (nitrate, nitrite and phosphate) and species relevant to the carbon cycle (carbonate, calcium and pH) is essential in open sea and coastal areas due to the fact that a control of the aquatic ecosystems is possible by the *in situ* reading of these species. The reasonably fast response times, small dimensions, simple operation, portability, and low energy consumption of potentiometric sensors make them attractive tools for this purpose. While potentiometric detection of carbonate, calcium and pH is possible in untreated seawater the large amount of sodium chloride in this sample (~600 mM) makes it difficult to determine nutrients. In this regard a desalination procedure is necessary in order to reduce the chloride amount in seawater up to mM levels. Additionally, hydroxide interference in nitrite and phosphate potentiometric detection can be suppressed by acidification of the sample.<sup>1</sup>

### The Fluidic System

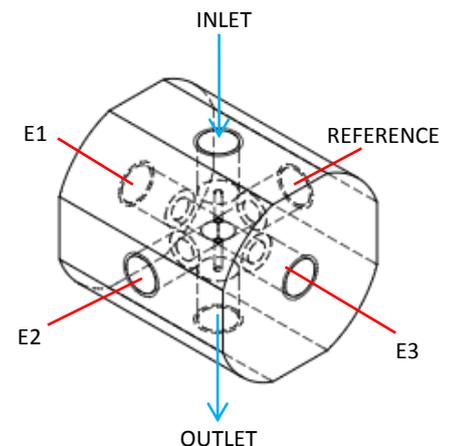
The fluidic system here proposed is composed of (in this order): 1) Potentiometric cell based on three indicator electrodes for carbonate, calcium and pH; 2) Desalination module; 3) Acidification module and 4) Potentiometric cell based on three indicator electrodes for nitrate, nitrite and phosphate and a reference electrode.



Scheme 1– Fluidic system.

### Potentiometric Sensors and Flow Cell

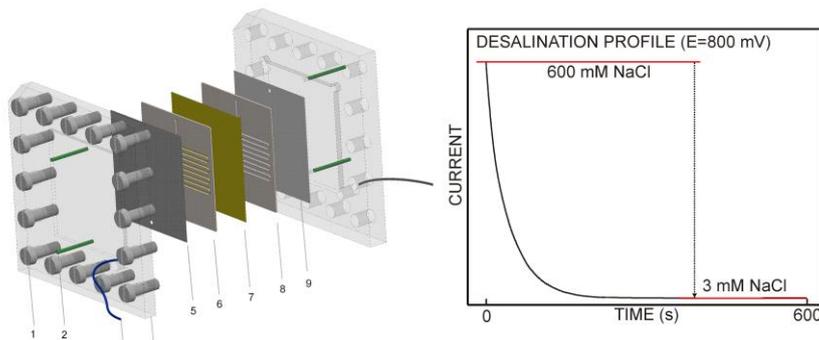
All-solid-state selective electrodes are based on lipophilic carbon nanotubes (f-MWCNTs) as transducing element deposited on glassy carbon electrodes.<sup>2</sup> Plasticized polymeric membranes are drop casted on the top of the f-MWCNTs film. The membranes contain the following selective receptors: Ionophore VII for  $\text{CO}_3^{2-}$ , Ionophore IV for  $\text{Ca}^{2+}$ , Ionophore I for  $\text{H}^+$ , tridodecylmethyl ammonium nitrate for  $\text{NO}_3^-$ , Ionophore VI for  $\text{NO}_2^-$  and uranyl salophene III for  $\text{H}_2\text{PO}_4^-$ . Glassy carbon electrodes are made by gluing carbon rods (2 mm diameter, HTW Germany) inside PEEK tubes and then the electrode surface is carefully polished. The Ag/AgCl reference electrodes are preparing with the same PEEK tubes using ceramic materials as the junction between the internal electrolyte (KCl sat. gel, Metrohm) and the sample solution. Then three electrodes and one reference electrode are placed in the flow cell (40  $\mu\text{L}$  of sample volume).



Scheme 2 – Potentiometric flow cell.

## Desalination Module

The desalination module is based on two serpentine channels (one for the sample and the other for the reference solution) made by natural rubber (6 and 7 elements) and separate by a cation exchanger membrane (7, FKL membrane). Each channel is in contact with either silver/silver chloride (5, reference solution) or silver (9, sample solution) foils acting as counter/reference and working electrodes respectively. All these elements are tightly closed between two Plexiglas blocks using several screws (1). Inlet and outlet for both channels are made through PEEK tubes. Each channel provides a sample volume of 150  $\mu\text{L}$ .

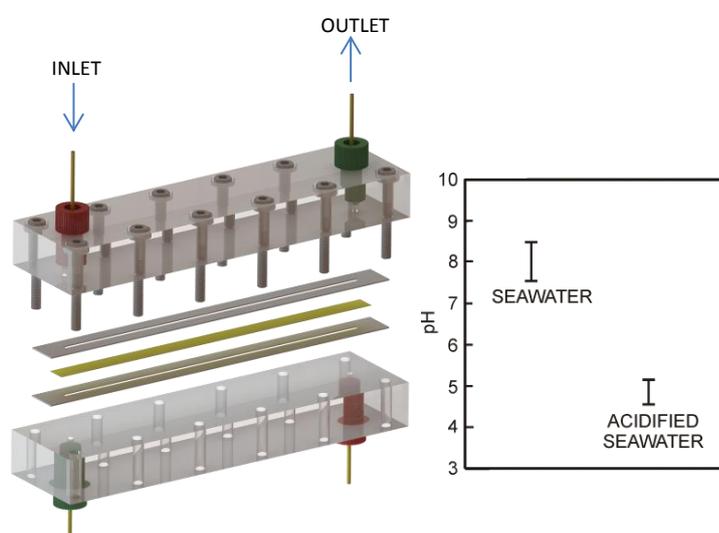


Scheme 3 – Desalination cell and current profile observed for the desalination of seawater.

*Electrochemical protocol for the desalination.* The applied constant potential of 800 mV between the two silver foils during 600-s results in the oxidation of Ag to  $\text{Ag}^+$  with the simultaneous incorporation of chloride from the sample to form a  $\text{AgCl}$  film. This process reduces the amount of chloride in the sample (seawater) up to mM levels (scheme 3, right).<sup>3</sup>

## Acidification Module

The acidification cell consists of two channels (one for the desalinated sample and the other for an acidic solution, 0.01 M HCl) separated by a cation exchanger membrane (FKL). These three elements are tightly closed between two Plexiglas blocks using several screws. A proton flow is established as concentration gradient from the acidic solution through the membrane to the sample solution. Desalinated seawater is acidified to a pH~5.



Scheme 4 – Acidification cell. Seawater pH after acidification process is ~5.

## Application in Seawater Analysis

Seawater is transported through the fluidic system by means of a peristaltic pump. First, the amounts of carbonate, calcium and pH are simultaneously determined in seawater using potentiometric sensors placed in the developed flow cell (scheme 2).<sup>1</sup> After that, the sample arrives to the desalination module in which the chloride amount is reduced up to mM level by applying a constant potential (Scheme 3).<sup>2</sup> Desalinated seawater is then transported to the acidification cell (Scheme 4). Here the pH of the desalinated sample is decreased to ~5. Finally, the levels of nitrate, nitrite and phosphate are determined. Limit of detections achieved with the potentiometric sensors are: 1  $\mu\text{M}$  for carbonate, 0.3  $\mu\text{M}$  for calcium, 1  $\mu\text{M}$  for nitrate, 0.4  $\mu\text{M}$  for nitrite and 10  $\mu\text{M}$  for phosphate.

## References

<sup>1</sup> N. Pankratova, M. Ghahraman Afshar, D. Yuan, G.A. Crespo, E. Bakker, ACS Sensors, 2016,1, 48-54.

<sup>2</sup> D. Yuan, A.H.C. Anthis, M. Ghahraman Afshar, N. Pankratova, M. Cuartero, G.A. Crespo, E. Bakker, Anal. Chem., 2015, 87, 8640-8645.

<sup>3</sup> M. Cuartero, G.A. Crespo, E. Bakker, Anal. Chem., 2015, 87, 8084-8089.

Eric Bakker, @ email: [Eric.Bakker@unige.ch](mailto:Eric.Bakker@unige.ch), University of Geneva (Switzerland)