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Electrochemical microsensor for in situ measurements of dissolved silicate in marine systems

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Long term monitoring and real time transmission of collected key-parameters of marine environments such as the macronutrients silicate, phosphate, nitrate… will allow to progress in our understanding of the ocean role in climate evolution and in its interactions with the terrestrial biosphere and anthropogenic activities. In order to achieve an in-situ miniaturized autonomous sensor, electrochemistry has been chosen for the detection and quantification of silicate in sea water.

Because silicate are non-electroactive species, a silicomolybdic complex is formed in-situ by oxidizing molybdenum metal to form molybdates and protons. To reach the needed acidic pH, a membrane is used to isolate the counter-electrode and avoid the reduction of protons formed. The complex is then detected on gold electrode surfaces by cyclic voltammetry or chronoamperometry. The detection limit is 1 μM.

On one hand, experimental parameters for molybdenum oxidation have been determined and tested on the 1st prototype developed. Even if the acidic pH is reached on the cell, it appeared a localised oxidation of molybdenum toward the membrane and the counter-electrode behind it. Therefore, homogenization of the solution and formation of the complex require too much time. A second prototype was then developed using 2 cells. The oxidation of molybdenum occurs in the first chamber then the complex formed is transferred into the second chamber to be detected on the gold electrode. Now, the molybdenum electrode, the membrane and the counter electrode have the same shape and the electric field is oriented in a vertical, unique, direction resulting in a homogeneous oxidation of the metal on its entire surface.

Results of experiments to evaluate the complexation time of silicates with this new prototype and the dilution effect when the solution is transferred to the detection cell will be presented.

On the other hand, we are trying to quantify silicate without standard addition or any calibration, using 2 gold working electrodes with different sizes. By solving Fick's diffusion equations to each electrode, it is possible to determine the silicate concentration and the diffusion coefficient. Experimental results show that depending on the silicate and molybdates concentrations or the pH of solution, different forms of silicomolybdic complex co-exist in solution. Preliminary results will be discussed.