

Electrochemical measurements : towards new *in situ* oceanic sensors

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Sulfide measurements

Potentiometric method

The detection is based on the equilibrium potentials of the second kind electrode **Ag/Ag₂S/S²⁻** (Kuhl *et al.*, 2000). Calibration curve has a theoretical slope of -29 mV/decade at 298 K. **Response time** is less than 1 s.

The study of the electrode evolution over three months has shown **good stability** in the response of these electrodes in the laboratory.

Voltammetric method

In this study, the silver electrode we proposed for medium to long-term use was shown to have a good linear behaviour from 200 μM to 20 mM, and with a stripping of 200 seconds at -0.45 volts, from 5 μM to 200 μM.

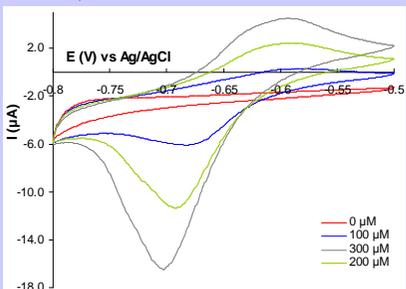


Figure 1: Sulfide response on silver electrode (blue = 100 μM, green = 200 μM, grey = 300 μM)

• It can be adapted for long term measurements with an autocalibration using the silver chloride oxidation on the electrode and the differences between the solubility constants of both compounds : AgCl and Ag₂S.

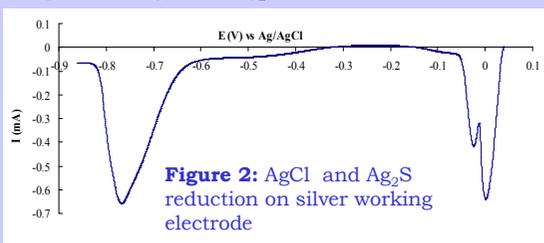


Figure 2: AgCl and Ag₂S reduction on silver working electrode

Collaboration:
Maurice Comtat, LGC-Toulouse,
Nadine Le Bris, Ifremer

Silicate measurements

Method

Silicates are **non electroactive species**. Their electrochemical detection is based on the formation of the complex, Si(Mo₁₂O₄₀)⁴⁻, formed in acidic solutions with molybdenum salts (pH 1.5). Voltammetry of this complex shows two reduction and two oxidation waves (Carpenter *et al.*, 1997).



• In the present work, we form molybdates directly in the medium to avoid the use of reagents, **oxidizing a molybdenum wire**:



• The acidification of the sample was obtained by the separation of the cathode and the anode to avoid the proton consumption at the former.

• The global reaction (oxidation and complexation) takes about 10 minutes. A linear response is obtained between 1 μM and 170 μM (with an accuracy of 3%) (Lacombe *et al.*, 2007).

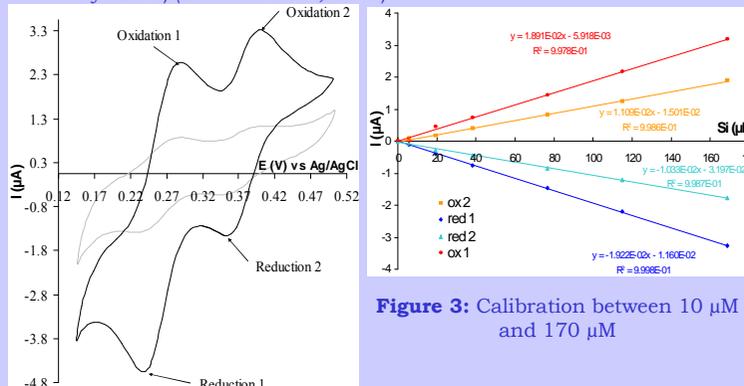


Figure 3: Calibration between 10 μM and 170 μM

Figure 4: Voltammograms with Si(OH)₄ = 10 μM (grey line) and 120 μM (black line) at 200 mV/s on vitreous carbon vs Ag/AgCl, Lacombe *et al.*, 2007.

In situ autonomous biogeochemical sensing in the marine environment is an immense challenge. The environment is harsh, dark, difficult to access, corrosive, subject to biofouling and characterized by large pressure, temperature, and ionic strength variations. However the precision and long term performance requirements are extremely high. Seawater is a complex matrix with many chemical compounds and biological species.

Submersible colorimetric analyzers for dissolved nutrients (silicate, phosphate and nitrate) in marine environments need significant energy and reagents, and their main drawbacks are their lack of autonomy, size and weight. Electrochemistry provides promising reagentless methods to go further in miniaturization, decrease in response time and energy requirements (Lacombe *et al.*, 2007, 2008). These microelectrodes integrated in silicon technology will allow to develop low cost, mass produced sensors.

Development of new sensors

MAISOE (STAE) :

« Microlaboratoires d'Analyses In Situ pour les Observatoires Environnementaux ».

Conception and implementation of an electrochemical method for nitrate determination and development of a silicate electrochemical microsensor.

Collaboration : LGC, LAAS, OMP

SENSEnet (Marie Curie Training Network) :

Development of microsensors for phosphate determination by electrochemical detection

Collaboration : LGC, LAAS, OMP, UNISENSE.

Industrial collaboration : ELTA/AREVA

Conception and development of chloride and phosphate sensors in complex aquatic media.

Collaboration : LGC.