

# SILICATES, PHOSPHATES AND NITRATES DETERMINATION BY AUTONOMOUS NUTRIENT ELECTROCHEMICAL SENSOR IN SITU - ANESIS

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## 1. ABSTRACT

Long term monitoring of marine environments requires *in situ* miniaturized autonomous instrumentation with the following figures of merit: lifetime, high precision, low detection limit, fast response time, good reproducibility, robustness, resistance to biofouling and high pressure, able of stable long-term operation, and low energy consumption. Real time transmission of collected data should be integrated and optimized. We present here the development of *in situ* nutrient analyzers performed at LEGOS /LGC, starting with wet chemical techniques (ANAIS-Autonomous Nutrient Analyzer *In Situ*) and then with electrochemical detection. Future routes of development are also provided.

## 2. RATIONALE

Monitoring the biogeochemical response of oceanic systems to environmental change is a key issue in understanding the vulnerability and resilience of marine ecosystems. Long time series of biogeochemical observations are crucially needed to understand the tight links between biological and chemical processes in environments subject to anthropogenic pressure. They are also essential to unravel feedback mechanisms in climate change. The oceans play a crucial role in the sustainable

future of humankind. They provide food, energy, minerals and the route for global transport. However, the immensity of the oceans remains largely undersampled in both space and time. The oceans are opaque to electromagnetic radiation, which inhibits the use of remote sensing beyond the surface. Water sampling is sparse, costly (~15-40 keuros ship/day), and subject to contamination. *In situ* sensors are the only solutions to this chronic undersampling. Physical sensors are currently used satisfactorily now due to many decades of research and testing. In contrast, biogeochemical sensors are in their infancy and are dominated by large, expensive, prototype devices requiring expert handling. Deployment of autonomous biogeochemical observatories requires improved sensing systems, which can operate reliably, with precision over long periods of time.

## 3. PRESENT DEVELOPMENT AT LEGOS/LGC

Sensors and analysers based on wet chemistry and electrochemistry techniques exist for a limited number of key-parameters of marine environments (e.g.  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , Fe, Mn, Si,  $\text{CO}_2$ ,  $\text{O}_2$ , pH). Prototypes of these systems have been widely used *in situ* for short-term deployments in various marine systems. At

LEGOS, an Autonomous Nutrients Analyzer *In Situ* (ANAIS) has been developed. Nitrate, phosphate, silicate are measured between 0 and 1000 m of depth when ANAIS is adapted on an eulerian YOYO profiling subsurface vehicle [1]. The ensemble YOYO-ANAIS nitrates was first deployed in the Western Mediterranean Sea offshore of the Blanes canyon (Spain) over a two weeks period with an acquisition of two vertical profiles of nitrates concentrations per day between 200 and 1100 m [2]. Within the CLIVAR/Confluence project, the same ensemble was then deployed from the Argentinean Research Vessel Puerto Deseado and operated during several weeks in the Southwest Atlantic ocean in the Malvinas current (41°S, 55°W). Twenty eight vertical profiles of nitrates concentrations were obtained between March 28 and April 19, 2003. Autonomous sampling occurred at 800, 700, 600, 400, 300, 200, 100 and 80m (Fig. 1) and two *in situ* calibration were performed per profile at the rest depth (800 m) and at the shallowest depth, 80 m. Data were recorded on Flash cards inside the YOYO body vehicle.

ANAIS nitrates alone was also deployed at a coastal site (Western Mediterranean Sea offshore the Bay of Banyuls sur Mer, France) at 23m depth on the SOLA mooring location between 2003 and 2005 within the framework of the SOMLIT (Service d'Observations en Milieu Littoral) network. Four measurements per day were acquired in order to obtain high frequency data (as compared to the regular field acquisition on site every other week). Episodic events such as the Rhone river high flooding discharge or sediments resuspension due to strong swell caused by intense southeasterly winds could be observed in the data record. Comparison with classical nitrates determination was excellent especially in the low concentration range between 0.1 and 0.8  $\mu\text{M}$ . However, submersible colorimetric analyzers for dissolved nutrients such as ANAIS require 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. Sulfide has been determined in sea water by different electrochemical methods [3]. First we developed potentiometric sulfide electrodes (based on an Ag/Ag<sub>2</sub>S electrode) that have been implemented from a submersible at 2300 and 3600 meters depth for short term measurements in a hydrothermal environment. Second we performed laboratory studies to set up a protocol with cyclic voltammetry (using Ag electrode) that could be more suitable for precise sulfide measurement in long term deployments. The voltammetric methods developed exhibited satisfying sensitivities for the broad range of concentration encountered in deep-sea chemosynthetic environments (from 5  $\mu\text{M}$  to 10 mM).

#### 4. RESULTS AND FUTURE

Silicate has been determined in sea water by different electrochemical methods based on the detection of the silicomolybdc complex formed in acidic media by the reaction between silicate and molybdenum salts. Cyclic voltammograms present two reduction and two oxidation peaks giving four values of the concentration and therefore increasing the precision. Then, chronoamperometry is performed on an electrode held at a constant potential. A complete reagentless method with a precision of 2.6 % is described based on the simultaneous formation of the molybdenum salt and protons in a divided electrochemical cell. Voltammetric detection of silicates was shown to be feasible within the range of concentration found in the ocean (between 0.3 and 160  $\mu\text{M}$ ) in about 6 minutes (Fig. 2). The detection limit is 1  $\mu\text{M}$ . The comparison of the voltammetric detection with the classical colorimetric analysis on seawater samples collected from the Drake Passage in the

southern ocean yielded an excellent comparison. This latter method is very useful for developing a reagentless sensor suitable for long term *in situ* deployments on oceanic biogeochemical observatories [4, 5]. The voltammetric method developed for silicate measurements is being adapted to determine phosphate concentrations over the concentration range found in the open and coastal oceans.

This effort will be performed within the ongoing RTRA (Réseau Thématique de Recherche Avancée) Midi Pyrénées within the framework of the STAE (Sciences and Technologies for Aeronautics and Space) Foundation. Indeed the MAISOE (Microlaboratoires d'analyses *in situ* pour des observatoires environnementaux) project aims to develop and test *in situ* microsensors in order to measure concentrations of elements (which may be present at trace levels) and to analyze their speciation. These studied elements may either act as nutrients (silicate, and nitrate here) in phytoplankton growth (marine systems and hydrothermal fluids) or be toxic such as mercury (continental systems). Since these natural systems are very complex and hostile due to their heterogeneity and extreme conditions, it is necessary to develop anticorrosion and antifouling protection in order to obtain relevant and accurate data over time, even in remote locations. The expected products from MAISOE will be prototypes of microsensors designed to quantitative detection of the selected components, in a first step at the laboratory scale with reference materials and in a second step in natural systems. These new instruments will be inexpensive, micro-designed and robust after implementation of the different functionalities. Silicon and polymer-based microtechnologies will be used to integrate electrochemical principles of phosphate detection in liquid phase. A phosphate microsensor will be developed within the framework of the ongoing Initial Training Network Marie Curie SENSEnet, led

by Dr Connelly from NOCS, UK. This 4-years long European combined effort will develop techniques for high performance *in situ* measurements of key biogeochemical parameters (e.g. phosphate and nitrate), pH, oxygen, carbon dioxide and reduced sulfur species. The technologies to be developed should be of course readily modified for use in a wide range of freshwater systems (cryosphere, lakes, rivers, groundwaters).

## 5. REFERENCES

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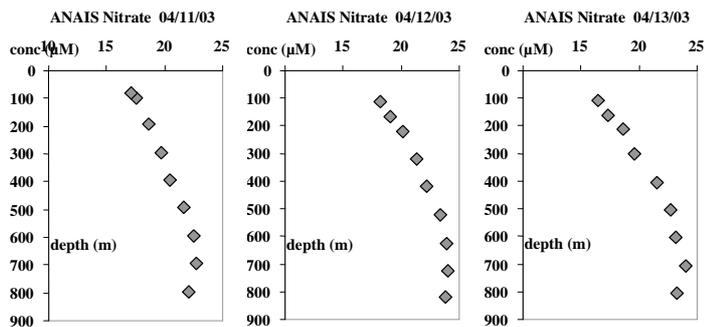


Figure 1: Series of vertical profiles of nitrate concentrations in the Malvinas Current (41°S, 55°W) with ANAIS

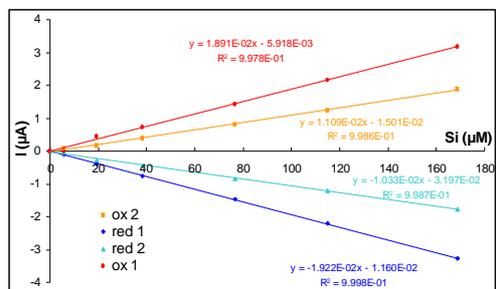
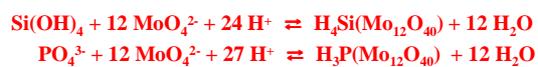


Figure 2: Silicates calibration with cyclic voltammetry within the range of concentration (0.3 to 160 μM) encountered in the open ocean.