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Electrochemical methods for autonomous chemical (phosphate and oxygen) monitoring in the ocean in the Oxygen Minimum Zone

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Oxygen Minimum Zones (OMZ), mainly localized in the EBUS, are known to play a crucial role on climate evolution via greenhouse gases budgets and on marine ecosystems (respiratory barrier, modifications of the nitrogen cycle). Deoxygenation will have widespread consequences due to the role oxygen plays in the biogeochemical cycling of carbon, nitrogen, phosphorus and other important elements such as Fe, S.
Developing new sensors for improving our understanding of the coupled biogeochemical cycles (P-O-C-N) in these regions constitutes an immense challenge. Electrochemistry provides promising liquid reagentless methods by going further in miniaturization, decreasing the response time and energy requirements and thus increasing our observing capacities in the ocean.
We present an electrochemical method for phosphate determination in seawater based on the anodic oxidation of molybdenum in seawater in order to create molybdophosphate complexes amperometrically detected on a gold electrode by means of amperometry or square-wave voltammetry. We propose a solution to address the silicate interference issue based on an appropriate ratio of proton/molybdate within an electrochemical cell using specialized membrane technology. The detection limit can be as low as 180 nM. An application of this method is presented in the OMZ offshore Peru. The results show excellent agreement when compared to colorimetry with an average deviation of 5.1%. This work is a first step to develop an autonomous in situ sensor for electrochemical detection of phosphate in seawater.
The STOX sensor for the measurements of ultra-low oxygen concentrations was improved by decreasing the distance between the sensing and guard cathodes. The modification of the sensor tip was done by development of a method for gold plating on the front silicone rubber membrane in order to form a guard cathode. Then, the traditional and modified STOX sensors were compared and the preliminary studies showed a great potential in STOX sensors with the modified guard cathode. The results show higher sensitivity and faster response time (t90 = 7.3 s) for the modified sensor. The temperature calibrations show an increasing signal with temperature (2.36 %/°C) similar for both sensor types. The improvement makes the sensor particularly suitable for use with CTD (Conductivity, Temperature, Depth) type instruments.