



## Comparative Assessment of Potentiometric and Voltammetric Sensors for Autonomous Monitoring in Deep Sea Sulfidic Environments

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Sulfur cycling is of major importance for the functioning of marine ecosystems, where microbial and chemically catalyzed redox processes involving this element play a key role in energy transfer. In situ measurements are necessary to understand the dynamics of metastable sulfidic environments, including hydrothermal vents, where concentration and chemical speciation can change within seconds as a result of chemical, biological and physical processes. The use of in situ electrochemical instruments for this purpose has several advantages despite some limitations inherent to the technique used.

Potentiometric sensors are characterized by small size, low-energy consumption, and low cost, which are attractive features for practical applications. The development of microelectrodes further improved the spatial resolution of these sensors. Compared to potentiometric sensors based on the measurement of equilibrium potentials without electrochemical consumption of the analyte, voltammetry is an electroanalytical method, which enables multi-species analysis by measuring oxidation or reduction currents of chemical species as function of the potential imposed to the electrode. Both methods were adapted for in situ measurement of sulfide at great depth, and further tested for autonomous monitoring over periods exceeding the usual duration of a few hours during submersible dive.

We used Ag/Ag<sub>2</sub>S potentiometric electrodes of 800  $\mu$ m diameter, consisting of a crystalline membrane of silver sulfide coating a silver wire. These electrodes are sensitive to S<sup>2-</sup>, so pH measurements need to be performed in parallel. In the voltammetric sensor, an Ag bare disc of 800  $\mu$ m diameter was used as working electrode that presented two response peaks to sulfide in two different levels of concentration. This fact allows the application of such electrode for experiments involving the analysis of a broader concentration range.

Both sensors have been deployed at 850m and 2500m depth along ~8-10 days in hydrothermal habitats of the Mid Atlantic Ridge and East Pacific Rise respectively, representing low (MAR - ~100 $\mu$ M) and high (EPR - ~1mM) sulfide concentration ranges. Potentiometric sensors displayed a good stability as defined from repeated calibrations during a series of dives and after longer deployment. Reproducibility was maximal over 100  $\mu$ M, therefore under this value the uncertainty can go up to 20 % which might still be reasonable for many issues. Attention must be given to the temperature dependence of electrode responses. Voltammetric sensors also showed good reproducibility after different dives and stability over more than one week deployment even though it must be confirmed for whole concentration range.

The relevance of potentiometric and voltammetric systems for (semi-)quantitative assessment of temporal changes of sulfide levels in deep sea habitats is demonstrated from these first results. Besides a need for discrete technical and operational optimizations, the information provided on the dynamics of such habitats is of high value to appreciate the reciprocal relationships between environmental conditions and associated faunal and microbial communities.

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