Sediment Microprofiler for NEPTUNE Canada

Introduction

Microsensors are very useful tools in the study of the biogeochemistry of marine sediments. Since their introduction in the 1970s, they have changed our view of the dynamics and complexity of sediment ecology. Their main advantage is that they acquire chemical information from a very small sediment volume and do this with very little disturbance of the sediment structure. Microsensors are typically electrochemical cells, in which one of the electrodes reacts specifically and (usually) reversibly with some chemical species. Currently, a wide variety of microsensors are deployed in making point-localized measurements of different parameters in the benthos, and new ones are still being actively developed. Microsensors at the Max Planck Institute for Marine Microbiology (MPIMM) are commonly used for experiments in aquatic ecology to measure pH, conductivity, oxygen, sulphide, temperature, ions, redox potential, etc.

The Sediment MicroProfiler (SMP) is an instrument that can host various types of microsensors. Microsensors, both electrochemical and optical, are attached to an assembly that can be moved up or down through the use of a linear positioning motor. This motion is usually performed in small steps of few tens of microns once the sensor tips are in the vicinity of the sediment, or inside the sediment depth. The SMP also has data loggers attached which captures the readout values of the amplifier electronics.

The SMP on Wally2, the benthic crawler, has several kinds of microsensors in its drive assembly. The various sensor types deployed in the September 2010 cruise are:

- **Oxygen Optodes**: Optical fibers can be modified into microsensors by coating the fiber tip with an active agent that reacts with a specific chemical agent, and produces a photochemical reaction such as fluorescence. The MPIMM builds its own oxygen sensors (See [2]) based on this principle. An excitation UV light is flashed on the oxygen-sensitive dye, which produces a fluorescent emission that is modulated by the amount of free oxygen available around the fiber-tip. Therefore, the oxygen concentration can be measured in terms of the phase and intensity of the fluorescent light.

- **Temperature Sensor**: This is an electrical PT1000 sensor to measure the temperature at the tip of the sensor.

- **Sulphide Sensor**: This is an electrochemical sensor that measures the concentration of sulphide S^{2-} ions. An iron-cyanide complex is used as the electrolyte that reacts with sulphide in the environment to produce a proportional amount of electrons at the anode. This sensor is constructed from a glass tube, and is painted black to avoid photo-poisoning of the electrolyte.

- **Conductivity Sensor**: This is an electrical sensor which measures the conductivity between two micro-electrodes. Comibining this information with the temperature and density, salinity is fairly easily calculated. This sensor provides interesting information without even such quantification, because the conductivity signal is a fairly reliable way of detecting the sediment surface.

- **pH Sensor**: The pH sensor is a membrane-based microsensor. It is a commercially available model, in which a membrane is coated with a specific ionophore. One side of the membrane is exposed to the sample, and the ionophores attach to H+ ions. This causes charge to build up on the sample side and the difference with the buffer pH within the reference of the electrode results in a measurable linearly proportional potential difference.

Making Measurements

Measurements can be made on these SMP microsensors using control software called **Sealand**, available from MPIMM. The software allows for measurement protocols to be written and executed by the control electronics in the SMP. Sealand can control the motor movements and read sensor data together and bundle it into a binary data file.

The motor moves the sensor into the sediment, but due to the fragile nature of these microsensors and their limited lifetime, they must be handled very carefully. The optical switch that interfaces with the oxygen optodes is custom-built at MPIMM and has specific guidelines to use it without damaging the instrument. Therefore, although collaborative experiments are welcome, the execution of the measurements will be handled by the MPIMM to minimize risk of damaging the sensors.

Microprofiler Data

The sensor outputs are connected to the digital channels in the following way:

Channel Number	Sensor
$0-6$	Oxygen phase
7	Oxygen reference intensity
10	Conductivity
11	Temperature
12	pH
14	Sulphide

The electrochemical sensors produce a millivolt (mV) or picoampere (pA) signal as their output, and a calibration of the individual sensor is required to convert the output into absolute concentrations.

The calibration for the pH sensor is performed as below:

$$pH = \frac{mV - 314}{\square 54 \square}$$

The calibration for the sulphide sensor signal into millimolars (mM) is performed as below:

$$H_2S = \frac{pA - 2.6}{\boxminus 36.389\sqsubset}$$

The temperature sensor provides a signal P which converts to temperature T in degrees celsius as:

$$T = 0.1 \times P$$

The calibration for the conductivity sensor is not required. The conductivity sensor is used here as a sediment surface detector. This is only qualitative information, as there is a sharp shift in the conductivity signal when the sensor enters the sediment. The shape of this curve can be used to estimate the location of the sediment-water interface.

The oxygen sensors are optodes, and the concentration information is present in the phase signal as explained above. To convert the phase and intensity signals of the optodes into absolute oxygen concentrations, the following calibration numbers are to be used.

[1] N.P. Revsbech and BB Joergensen, "Microelectrodes: their use in microbial ecology", Adv. Microb. Ecol, vol. 9, pp. 293-352, 1986.

[2] Klimant, I. and Kühl, M. and Glud, RN and Holst, G., "Optical measurement of oxygen and temperature in microscale: strategies and biological applications", Sensors and Actuators B: Chemical, vol 38, 29—37