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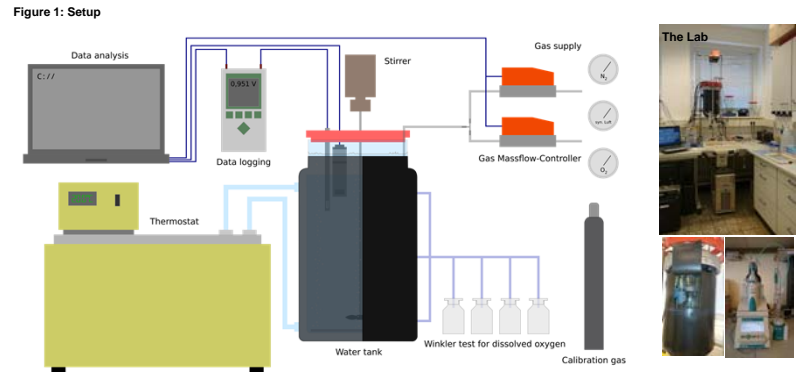
## Introduction

Dissolved oxygen (DO) is an important biogeochemical parameter, which is used as an indicator for photosynthetic activity of phytoplankton and for calculation of primary production. For this reason, oxygen sensors are used frequently in oceanographic studies. They are integrated in different in situ measurement systems like FerryBoxes, profiling probes, floats, etc. Measurement of high quality and accurate oxygen values requires a precise calibration of each sensor. Optodes, which are widely used oxygen sensors, need a multipoint calibration, because their measurement method is temperature sensitive.

## Setup multipoint calibration system

### Components

Optodes or other dissolved oxygen sensors are placed into a temperature controlled water tank. This water tank is light proof, because optode foils with fast response are light sensitive and can be changed by direct light exposure. Water is bubbled with a constant ratio of nitrogen to artificial air (controlled via flowmeters) to keep dissolved oxygen at a stable and reproducible saturation level over a long time period. A stirrer mixes the water inside the water tank to provide homogeneity. Simultaneously with the optode oxygen measurements taken at different temperature and saturation steps, discrete water samples are drawn and analyzed in the lab by Winkler titration. The measured Winkler values are then used to generate a multipoint calibration matrix, which is used to calibrate the optodes.



## Application

### Method for Multipoint DO Calibration

Mass flow controller is used to set different saturation levels of oxygen at a constant temperature. After a while, when saturation is stable, replicate samples are drawn for Winkler titration measurements. This step is repeated at every calibration point. In the end, a matrix of different saturations and different temperatures is generated. The matrix values are then used to calculate the optode foil coefficients.

The generated matrix of calibration points can be used to characterise any DO sensor that is being tested. Figure 3 shows for example the relative difference (Delta, %) between Winkler probes and two different optode measurements.

### Validation of Field Measurements

The results of the multipoint measurements can be used to validate field measurements after instrument retrieval.

The correlations between the Winkler probes and optode measurements obtained are used to recalculate the field measurements. For example, during deployment discrete water samples for Winkler analyses taken in the field can show that the optodes are underestimating dissolved oxygen (Fig. 5). In this case the field Winkler probes cannot be used for correction, because the number of the samples is too low to generate a proper correlation between Winkler probes and optode values. However, using the laboratory generated correlation (Fig. 4), we were able to correct the optode measurements (Fig. 5).

### Intercalibration

The multipoint calibration method also allows for comparing different kinds of sensors. When tested under the same conditions in the lab, the combination of Winkler to sensor, and sensor to sensor calibrations can be used to validate sensor performance and field data.

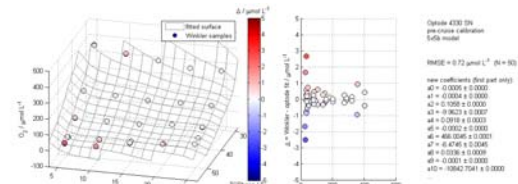


Figure 2: Fit of the optode foil coefficient matrix (by Craig Neill, script from H.Bittig), based on equation by Garcia & Gordon (Oxygen solubility, 1992)

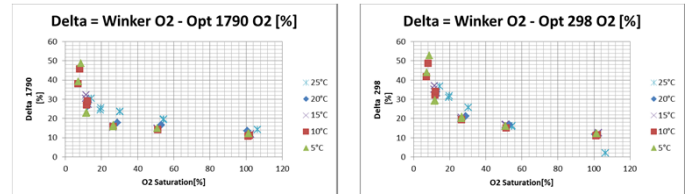


Figure 3: Relative difference between Winkler and optode measurements (SN1790 and SN298) of dissolved oxygen.

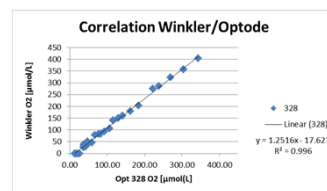


Figure 4: Laboratory multipoint measurement

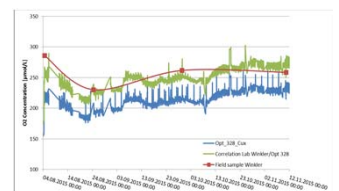


Figure 5: Field measurements FerryBox Cuxhaven

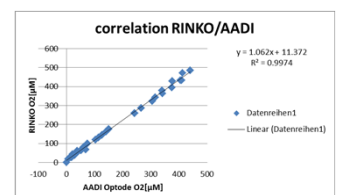
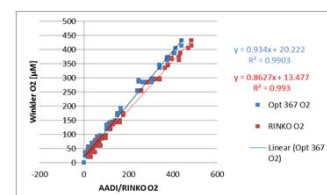


Figure 6: Comparison between different DO optodes: RINKO and AADI. Correlation with Winkler probes (left), and correlation between RINKO and AADI measurements (right)

## Conclusion

This multipoint DO calibration method is developed to calibrate dissolved oxygen sensors and is useful to evaluate and correct continuous monitoring data in different oceanographic applications, including FerryBox monitoring platforms. It is an essential tool that allows to keep data quality of dissolved oxygen measurements high. Its use is complex and time consuming. To optimise the analysis time, Winkler probes can be replaced with dissolved oxygen sensors, which are carefully calibrated.