Contribution of chemometrics to In Situ Mass Spectrometry data processing

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1 Introduction

In situ analyses are becoming a more and more common in ocean sciences as they present the double advantage of providing continuous datasets and avoiding samples contamination through air or on board manipulation. Even if mass spectrometry can be considered as an old and well-known technics, its application to in situ analysis of dissolved gas using a hydrophobic polymer membrane as an interface between the device and the environment is more recent[1]. Unfortunately, very little data is available to calibrate such in situ mass spectrometry (ISMS) based instruments.

Calibrating a mass spectrometer for gas measurement is not in itself a challenge, as the response of the instrument is a linear response of gas concentration. However, adding a membrane to this equation leads to a more complicated relationship, because the permeability of the latter depends on many factors[2]: hydrostatic pressure (up to 600 bars when considering deep ocean in situ application), gaseous species considered, temperature, salinity, fouling, aging, etc. This entails the need to model each parameter one by one and can thus induce several days of experimentation. Here, we rather chose to use a field ISMS datasets and apply chemometric pretreatments and models to it in order to establish a calibration model for the instrument.

2 Material and methods

The field dataset has been acquired during a monitoring cruise on the neo volcanic area offshore Mayotte (MAYOBS 15). The gas concentrations (CH_4, CO_2 and H_2) were determined on-board by reference methods[3,4] on samples collected by CTD-rosette deployments, whereas O_2 concentrations were in situ measured by a calibrated optode (Aanderaa 4831F, frequency 1Hz) mounted directly on the CTD. The In Situ Mass Spectrometer (ISMS) was deployed on each CTD/rosette operation during downcast and upcast operations thus covering all the sources of signal variations encountered in the natural environment. Chemometrics pretreatments and calibration models have then been explored in an attempt to establish a calibration model for the ISMS from the discrete data.

3 Results and discussion

Several pretreatments[5,6,7] and combinations of pretreatments usually used for mass spectrometry signal corrections and normalizations have been tested without any relevant result. Results showed that classical workflows were unsuitable for this application. The use of block scaling, including a physical parameters block (pressure, temperature, salinity, etc.), coupled with local methods of calibration[8] yield to conclusive calibration models (Figure 1). This latter can be completed after each new cruise, to build increasingly robust models.

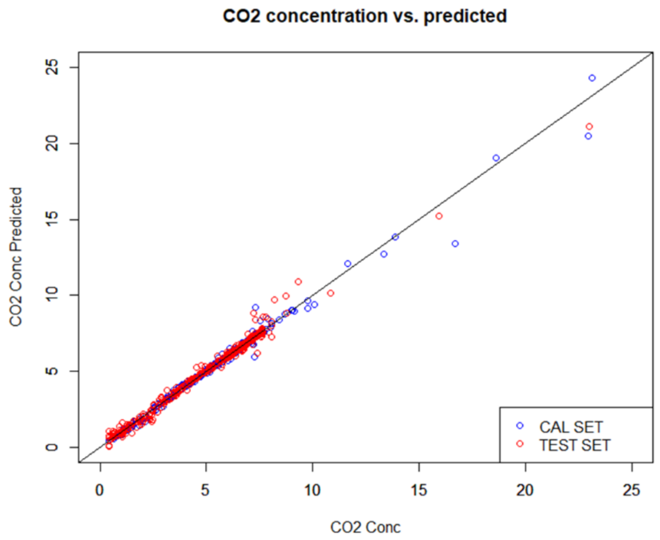

Figure 1: Predicted vs. Observed values for the CO_2 calibration model

4 Conclusion

The present work has shown that 1) the application of specific spectral pretreatments and 2) the use of appropriate chemometrics models, allow overcoming the issues linked to the in situ mass spectrometer and its membrane behavior during a water column vertical profile.

Oxygen, methane, carbon dioxide and hydrogen concentration profiles in underwater neo-volcanic context have therefore been established and compared to reference methods results based on water sampling followed by their gas concentration analysis (H_2, CH_4 and CO_2).

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