OPTIMIZATION OF A MEMBRANE BASED NDIR-SENSOR FOR DISSOLVED CARBON DIOXIDE

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ABSTRACT

The autonomous measurement of dissolved carbon dioxide (CO_2) is of great and still increasing importance for addressing many scientific as well as socio-economic questions. Although there is a need for reliable, fast and easy-to-use instrumentation to measure the partial pressure of dissolved CO_2 (pCO_2) in situ, only few autonomous underwater sensors are available.

Here we present the measuring principle as well as the latest development state of a commercial sensor (HydroC™/CO2, CONTROS Systems & Solutions GmbH, Kiel, Germany), which is optimized in a collaboration between the IFM-GEOMAR and the manufacturer. In situ tests and laboratory experiments are essential parts of the comprehensive optimization process, which aims at the successful autonomous long-term deployment on e.g. surface buoys, underwater observatories and floats.

1. INTRODUCTION

The partial pressure of carbon dioxide (pCO_2) is one of the four measurable parameters defining the marine carbon system. Its long-term measurement is crucial for the understanding and monitoring of many biogeochemical processes in the ocean on various time-scales and spatial extends [1]. The rising atmospheric concentration of the green-house gas CO_2 caused by anthropogenic influences, such as the burning of fossil fuels [2], has an impact on world's climate. In this respect the oceans play a key role, since they act as a major sink for the CO_2 [3]. As a consequence to the increase in dissolved CO_2, more carbonic acid is formed and the pH value decreases [4]. This effect, referred to as ocean acidification, affects calcifying organisms as well as reproduction and physiology of other species [5]. By looking at its influence on climate and acidification the issue of in situ pCO_2 measurements extends from scientific towards social importance. By considering the issue of marine sequestration of CO_2 as medium-term mitigation option to counteract increasing CO_2 emissions [6] the monitoring of pCO_2 even extends its scope from social to economical aspects.

The diversity of measuring motivations is reflected in the amount of available platforms for the installation of pCO_2 instrumentation. Research vessels or voluntary observing ships (VOS)/ships of opportunity and surface buoys are currently the main platforms for long- and short-term surface water pCO_2 measurements. Moorings, lander and buoys are platforms for long-term underwater installations. As a payload on mobile platforms such as remotely operated vehicles (ROVs), autonomous underwater vehicles (AUVs) or crawlers, pCO_2 sensors can be used for short-term mission based monitoring and measuring of dissolved CO_2. The installation of respective instrumentation on drifting floats combines both, long-term measurements and mobility [7].

Up to date only few autonomous underwater in situ sensors are available [7][8]. Within a collaboration of the IFM-GEOMAR and a manufacturer for underwater gas sensors (CONTROS Systems & Solutions GmbH, Kiel, Germany) a commercial pCO_2 sensor (HydroC™/CO2) is developed further. The instrument is optimized to meet the needs resulting from the diverse fields of application as well as platforms.

The optimization work is currently in the state of accuracy and precision assessment by means of different in situ deployments. The data analysis and processing is under close investigation.

2. THE SENSOR

Like most surface water underway pCO_2 instruments [9] the HydroC™/CO2 (Fig.1) measures the concentration of CO_2 in an equilibrated gas stream by means of a non-dispersive infrared detector (NDIR-detector), in which the CO_2 concentration is optically determined on the principle of absorption spectrometry. The wet air within the sensor's internal gas stream circulates between the detector and a membrane equilibrator. The latter is integrated into the head of the sensor and consists of a flat hydrophobic silicone membrane acting as a semi-permeable phase boundary between the water and the inner gas circuit of the sensor. A continuous gas flow is maintained by a pump. Additional sensors for temperature, pressure and humidity within the circuit are necessary for a proper analysis and data processing. The measuring values of the NDIR unit and the data of the additional sensors are settled and either internally logged or parsed via cable connection.

As shown in Fig.1 the sensor is of a tube shaped design and of moderate dimensions. The depth capability ranges from 2000 to 6000 m depending on the model. The power consumption depends on the water temperature and it is typically around 3-4 W at 10 to 32 V during operation with stabilized temperature and less than 10 W during the warm-up period, which is typically not longer than 30 min. The measuring range of the sensor is either 200 – 1000 ppmV, 200 – 3000 ppmV or 200 - 5000 ppmV for CO_2 in the gas phase ($xCO_{2,gas}$).

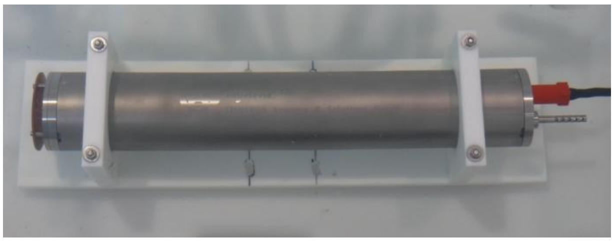

Figure 1. HydroC™/CO2 within a POM mounting. The sensor head is on the left. Cable connection and an external temperature probe are on the right end of the tube. The titanium housing is 90 mm in diameter and sensor has an overall length of 550 mm.

3. OPTIMIZATION APPROACH

The optimization work on the instrument is carried out in a logical order leading to a circuit of tasks. A schematic of the optimization methodology is depicted in Fig.2.

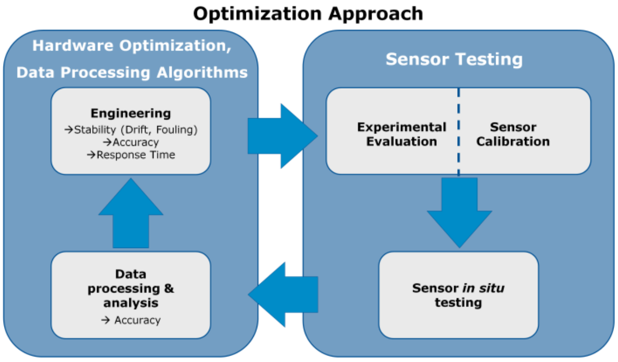

Figure 2. Optimization methodology.

The process starts with hardware optimization that comprises different engineering tasks covering membrane investigations, optimization of the optical unit as well as changes and adaptations in the internal overall design. As a next step the sensor is tested and calibrated within a laboratory setup. In situ tests provide necessary field data and show pros and cons of the instrument. This step is followed by the optimization of data processing algorithms and analysis. At that point the circuit is closed and the process starts again with hardware optimization. The methodology is followed until the sensor shows the aspired performance within in situ tests.

3.1. Engineering

All the tasks related to the hardware optimization of the sensor affect the main performance properties of the instrument and are thus of great importance.

One of the key elements is the optical NDIR unit. Its performance dominates the accuracy of the entire sensor. Since the response behavior of the IR detector is temperature dependent, the entire NDIR unit is temperature stabilized within the sensor. As an additional back-up the NDIR unit with its IR detector and the corresponding electronics is temperature calibrated. Mainly due to changes in the intensity of the light source with time, NDIR detectors are prone to signal drift. To account for this unwanted effect the optical unit combines a two-beam setup with repeated zero point calibration. The two-beam setup makes use of a reference channel, which measures the intensity at a wavelength that is not exciting CO_2 vibrations and which can thus be used for continuous drift correction. The repeated zero point calibration or zeroing is carried out in adjustable and discrete time intervals (typically 12 or 24 h) during long deployment periods. For some minutes the gas within the sensor's circuit does not pass the membrane but a soda-lime column instead, which converts and thus removes the CO_2 from the sample gas. In addition to its drift correction function, the zeroing can be used for an in situ performance test of the sensor; as soon as the zeroing is over, the sensor signal displays the actual response characteristics of the unit at the very in situ conditions.

The membranes used with the sensor are either composite or mono-layered silicone membranes with an effective layer thickness of around 10 µm. The thinner the dense material, the higher is the permeability and the shorter is response time of the sensor. It remains to be assessed in how far fouling on the membrane affects the stability of the sensor signal and to which extend membrane hysteresis effects can be observed during deepwater measurements.

Beside the membrane the internal overall design of the sensor influences the response time. The gas volume is minimized; connectors and different tubing materials are tested. Insulation and temperature stabilization are addressed, since they can influence the stability of the instrument. One prototype features a total of 6 additional sensors for the measurement of temperature, humidity and pressure at different positions within the gas circuit and an extra temperature probe for sea water. These sensors are both, essential for proper pCO_2 measurements and necessary to understand the processes happening in the instrument during the time of deployment.

3.2. Sensor Testing

For the investigation of the overall sensor response behavior as well as for a direct reference calibration and for experimental testing purposes, a calibration setup is used. The water within a 150 L insulated tank is temperature controlled ($\Delta T < 0.05$ °C) within 0 to 30 °C. As a filling we use pure water with carbonate additives to mime the buffering effects within ocean water. Silver ions are used as an anti-foulant. Water is continuously pumped through a reference $p\mathrm{CO}_2$ underway system [10], which uses a bubble-type/laminar-flow equilibrator and is equipped with a NDIR detector (LI-COR®, Inc., Lincoln, Nebraska USA). Adjustments of the pH-value by injection of NaOH or HCl solutions allow for the realization of a wide range of CO_2 concentrations ($xCO_{2,\ gas}$) of up to 3000 µmol / mol.

For calibration the sensor is placed in the temperature stabilized water tank. The reference system provides the $p\mathrm{CO}_2$ of the tank water. Equilibration following Henry's law is assumed to take place within the sensor's membrane head. The actual mole fraction of CO_2 present in the sensor can be derived. The corrected NDIR detector signal of the sensor is calibrated against the obtained reference xCO_2.

Carrying out a calibration of the sensor with dry standard gases is easier, makes fewer demands on instrumentation and is much faster compared to a complete tank calibration (~1 h vs. ~6 h). Furthermore, possible sources of error on the side of the underway reference measurement are minimized and the long calculation chain within the analysis of the reference system's data with its multiplication of measuring errors falls away. In return a gas calibration requires a proper understanding and mathematical consideration of the thermodynamic processes occurring in the sensor, especially in the gas circuit, and of all the interactions affecting the IR measurement. Furthermore it is only applicable if the equilibration properties of the membrane equilibrator are sufficiently understood [7] and described. We aim at achieving congruent calibration polynomials by tank and dry gas calibration with a maximum difference in $xCO_{2,gas}$ of less than 10 µmol / mol.

Currently in situ deployments of the sensor are under way. It is participating in an official technical demonstration carried out on surface buoys [11] and it is used on board RV Polarstern within an inter comparison exercise. These measurements will provide useful information regarding the sensor's stability as well as accuracy with respect to the tank calibration.

3.3. Data Processing and Analysis

Data processing and analysis of the NDIR detector's as well as the additional sensor's data is closely linked to the calibration procedure as far as the sensor's overall accuracy is concerned.

So far the absorption of IR light following Lambert-Beer's law is properly considered including the pressure, temperature and humidity influence on the actual gas concentration within the sensor.

As a next step the effects of pressure broadening and real gas interactions will be included into the analysis. Those become especially important when dealing with high partial pressures.

4. CONCLUSION AND OUTLOOK

We presented an optical underwater sensor for dissolved CO_2, which by its design and size lend itself to usage within various fields of application and on multiple platforms. The explanation of the applied optimization procedure was emphasized. Hardware sided all requirements are met for a proper assessment of accuracy as well as reliability, which will follow from multi-referenced in situ tests. After their analysis the optimization circuit for the sensor will be restarted at the point of engineering with a focus on the sensor's response time.

The calibration procedure will be further optimized and a proper mathematical consideration of all relevant effects is aimed at. The latter is necessary for a strengthened investigation of a pure gas phase calibration of the sensor.

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