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Development of a novel hybrid pH sensor for deployment on autonomous profiling platforms

V. Rérolle¹, D. Angelescu¹, A. Hausot¹, P. Ea¹, N. Lefèvre², C. Provost², M. Labaste²

1.Fluidion SAS, 75001, Paris ,France

2. Sorbonne Universités (UPMC, Univ Paris 06)-CNRS-IRD-MNHN, LOCEAN Laboratory, 75005, Paris, France
v.rolle@fluidion.com

Abstract— Ocean acidification is a direct consequence of the atmospheric CO₂ increase and represents a threat for marine ecosystems, particularly in the Arctic. High-quality seawater pH measurements with good spatial and temporal coverage are required to apprehend the ocean acidification phenomena. We are working to develop a high-accuracy, high-resolution pH sensor that has the potential to allow global ocean acidification mapping through deployment on fleets of ARGO floats and other autonomous platforms already in existence. The instrument implements a novel hybrid approach, utilizing the two different and complementary measurement techniques (potentiometric and colorimetric) to generate temporally dense and highly accurate pH data. Here we present the concept and initial results obtained from a hybrid pH sensor. Results show that the potentiometric part of the sensor is capable to operate in real ocean pressure and temperature conditions, including near-freezing temperatures typical of Arctic environmental conditions. The colorimetric part provides a stable reference to perform periodic recalibrations and remove drift.

Keywords—Hybrid pH sensor, microfluidic, colorimetric, electrode, acidification.

I. INTRODUCTION: STATE OF THE ART

Ocean acidification, a direct consequence of CO₂ increase in the atmosphere, represents a real threat for marine ecosystems [1], the Arctic Ocean being the most vulnerable region with the strongest pH decrease [2,3]. High-quality seawater pH measurements with good spatial and temporal coverage are required to understand ocean acidification phenomena. While several ocean parameters can now be measured globally thank to a network of autonomous profiling and drifting floats [4], pH is a notable exception: there are currently very few direct pH measurement options available, despite efforts to develop a continuous accurate pH measurement system by several academic and industrial groups [5,6,7]. As a consequence, long-term trends in surface pH are often inferred only indirectly from other measured ocean carbon system parameters. The oceanographic community is currently in need of autonomous pH sensor technology that will affordably, accurately and efficiently measure ocean chemistry from its shallowest to its deepest waters even in remote areas with extreme conditions.

Installation of sensors on profiling and drifting floats requires a small, solid and lightweight sensor capable of performing highly accurate measurements, with fast response time and without significant measurement drift for extended deployment durations. Cost is also an important consideration, since profilers stop emitting their location at the end of battery life, making very unlikely the prospect of their recovery. Traditionally, seawater pH has been measured using one of two standard methods: potentiometry (pH electrodes) and colorimetry (using pH indicators), which remains the gold standard in the field [8]. A third method, using MOS field effect transistors (MOS-FET), has recently been adapted to marine waters, and was only recently released as a commercial solution for surface and potential profiling applications [9]; this new sensor can be categorized under potentiometry.

Every type of traditional ocean pH measurement presents a set of advantages and disadvantages. Colorimetry, for example, is well adapted to many biogeochemical parameters because it enables high-quality measurements with low detection thresholds and without drift or need for periodic recalibration. It allows the acquisition of quality data in a wide range of temperature and salinity environments, with negligible deterioration in measurement quality even after long periods of use (> 1 year). The colorimetric method does however consume liquid pH indicator (m-cresol purple being routinely used in ocean monitoring), which limits the total number of measurements available as well as their frequency. Colorimetric sensors require metered reagent dosage and accurate optical measurements that are not always easy to achieve in actual field conditions or during profiling operations [10].

The potentiometric method, meanwhile, does not require use of reagent. Potentiometric sensors (electrodes) are more easily miniaturized, consume little energy and enable continuous measurements with fast response times. Therefore, this method allows vertical profiling. However, these sensors can be very sensitive to electromagnetic perturbations or to changes in temperature and salinity, with phenomena such as electrolyte diffusion and biofilm formation further leading to frequent recalibration requirements that are impossible to accomplish on a drifting float. There is consequent reluctance within the ocean

acidification community to deploy stand-alone electrode-type sensors for extended periods without human intervention.

The recently developed MOSFET-based sensors show a relatively good stability but require intricate and lengthy location-dependent calibration procedures and still suffer from measurement drift after several weeks of deployment, requiring data correction [11].

The paper presents the concept and initial results obtained from a novel hybrid pH sensor using a combination of potentiometric and colorimetric measurements to compensate for drift and generate high-frequency and accurate ocean pH data. Our aim is to develop an accurate (≤ 0.010 pH units) and precise (0.001 pH units) high-resolution pH sensor that has the potential to allow global ocean acidification mapping through deployment on fleets of ARGO floats and other autonomous platforms already in existence. The instrument implements a hybrid approach, utilizing the two different and complementary measurement techniques (potentiometric and colorimetric) to generate temporally dense and highly-accurate pH data. The hybrid system is ultimately aimed to be deployed on an autonomous platform and will ensure the precise re-calibration of the potentiometric electrode by the periodic colorimetric measurements performed throughout the duration of the platform deployment.

We will start by characterizing a standalone electrode before presenting an initial ferry-box version of the hybrid sensor for continuous underway measurements, and then present a new version of the sensor that is adapted to surface water monitoring on moorings (currently under test). Results show that the potentiometric part of the sensor is capable to operate in real ocean pressure and temperature conditions, while the colorimetric part provides stable reference to perform periodic recalibrations and remove drift. Future work will focus on adapting the colorimetric analyzer housing for in-situ deployments at depth, with the ultimate goal of deploying the hybrid pH setup on autonomous drifting and profiling platforms deployed in the Arctic Ocean.

II. INSTRUMENTS AND METHODS

A. Instruments

1) Potentiometric sensor

The potentiometric sensor is a combined glass-electrode and a reference electrode (Ag/AgCl) in KCl gel. The potentiometric sensor uses an instrumentation amplifier circuit – whenever referred to in text, the electrode voltage refers to the amplified signal. The potentiometric sensor can be outfitted with either a plastic or a stainless-steel casing, depending on weight constraints and on possible presence of electrical interferences, and can perform high-frequency measurements (1 Hz) from surface to 2000 m depth in seawater and brines solution with temperature ranging from -2 to 60 °C.

2) Colorimetric analyzer

The colorimetric analyzer is based on the widely used metacresol purple (mCP) indicator for seawater pH measurement [12]. The pH indicator is added to the seawater and optical spectra are recorded using a combination of LED light sources and a spectrophotometric detector, absorbance measurements being performed at 434, 578 and 700 nm. A fluidic manifold integrates a pressure control block for reducing the underway supply pressure to 6 PSI, electro-fluidic valves for controlling the flow of sample and reagent streams, a micromixer manufactured using micro-electromechanical systems (MEMS) technology and implementing the flow-folding principle, as well as MEMS hydraulic resistors for controlling flow rates throughout the microfluidic geometry. The fluidic manifold enables precise control of the reagent and sample dosage and mixing prior to injection into a custom MEMS silicon/glass 25mm-long optical cell. Coupling of the optical cell to LEDs and detector is achieved via optical fibers. A dead-end glass microfiber filter (5 μm porosity) is used to retain particles that may be present in the sample, prior to injection in the fluidic manifold. The colorimetric analyzer can be programmed to perform periodic measurements at intervals ranging from 5 minutes to several hours, depending on deployment requirements.

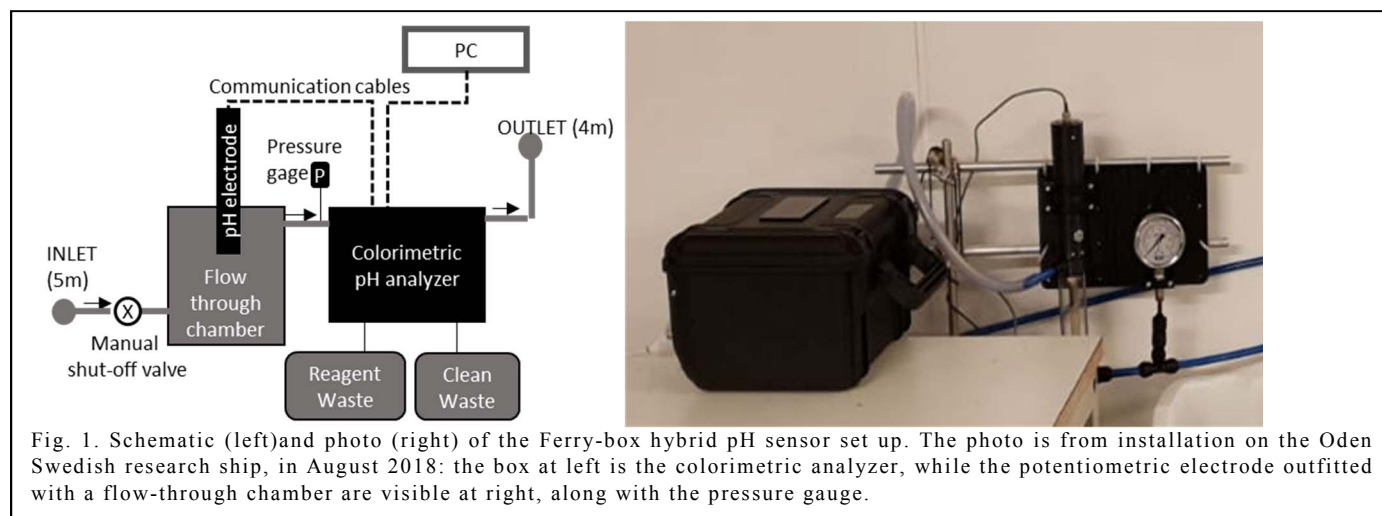


Fig. 1. Schematic (left) and photo (right) of the Ferry-box hybrid pH sensor set up. The photo is from installation on the Oden Swedish research ship, in August 2018: the box at left is the colorimetric analyzer, while the potentiometric electrode outfitted with a flow-through chamber are visible at right, along with the pressure gauge.

3) Hybrid pH instrument and Ferry-box set up

The first hybrid pH instrument presented in this work is adapted to ferry-box measurements, and is a combination of the potentiometric sensor and the colorimetric analyzer. The hybrid instrument is a stand-alone unit: it can operate on battery or mains power if present, is configured via an integrated LCD screen and two push-buttons, and all data (colorimetric and electrode) are logged internally or, optionally, uploaded to the cloud if cellphone network is present. A Java interface is used for live data observation, data retrieval over USB after long-term deployment, and electrode calibration.

The hybrid sensor is installed in-line on the ship's underway water supply: seawater flows initially to the electrode via its flow-through chamber and then to the colorimetric analyzer, where a few mL are diverted for spectrophotometric measurement (see Fig. 1 – the actual measurement is performed on 1.6 μ L). Sample temperature is measured at two places: within the electrode flow-through chamber and at the analyzer's optical cell.

4) Surface buoy hybrid system

The ferry-box hybrid system was modified to enable its deployment on data buoys. In this configuration, the electrode is deployed directly in-situ under the buoy while the analyzer is installed on the buoy. Seawater sampling for the colorimetric measurement is performed from the electrode location using a peristaltic pump connected to a length of tubing (See Fig. 2, left). A tangential filtration system has been developed to replace the dead-end filter for long-term and turbid water deployments. The electrode is outfitted in this case with a 316 stainless steel electronics housing to avoid electromagnetic interferences from other equipment that may be present on the buoy. Data are logged internally but also communicated remotely to cloud data servers in real time via a GSM cellular link.

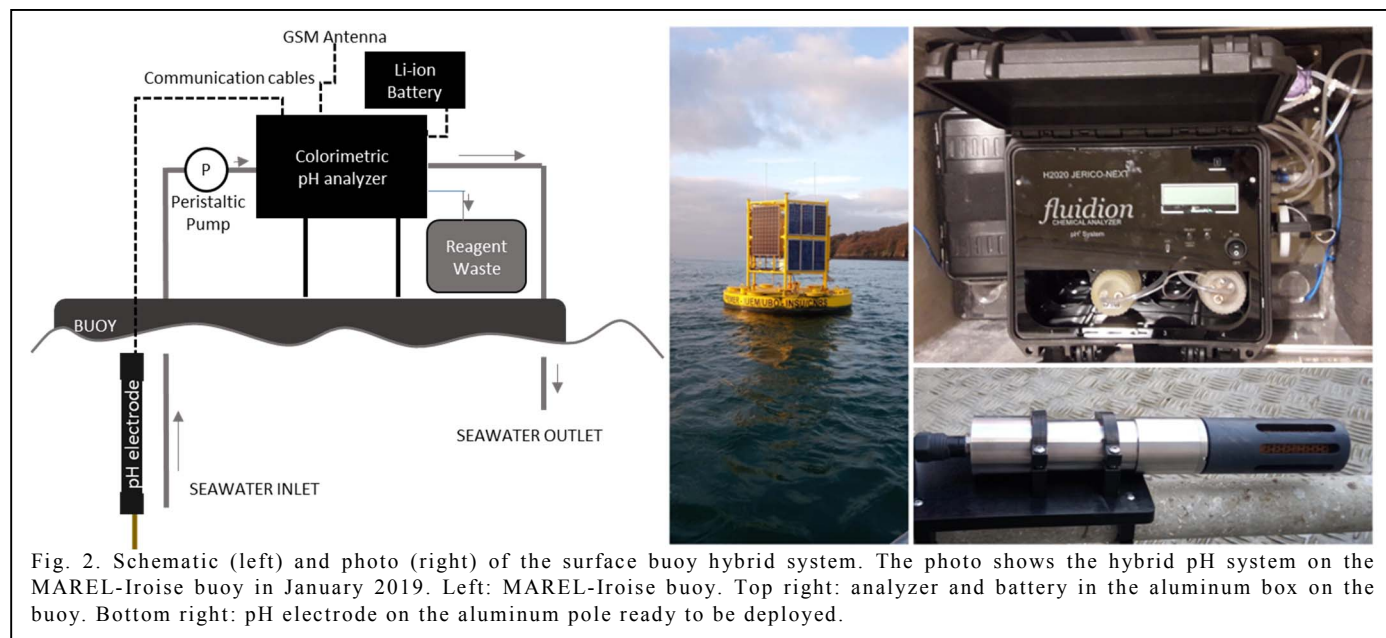
The hybrid pH system was deployed on the MAREL-Iroise buoy at the entrance of the Bay of Brest (France, Brittany) on the 9th of January 2019 (Fig. 2, right). MAREL-Iroise is one of the scientific buoys of the French network for monitoring of coastal environment (COAST HF). Since year 2000 this buoy has been autonomously providing seven core parameters (conductivity, temperature, dissolved oxygen, turbidity, chlorophyll fluorescence and pH) of the marine environment, measured every 20 minutes at a depth of 2.5 m.

B. Methods

1) Chemical preparation and bench-top calibration protocol

The purified 2 mM *meta*-Cresol purple (mCP) indicator solution is prepared in 0.7 M NaCl solution at pH \approx 8.0. mCP purification is performed by flash chromatography following the protocol detailed in [13]. Tris buffer solutions at different pH are prepared in artificial seawater according to the protocol described in [14].

pH values of buffer solutions are determined by manual bench-top colorimetric measurements using the Standard Operating Procedure (SOP) [15] and applying purified mCP characterization coefficients from [16]. Temperature of the solution is measured just after recording the absorbance spectra with a hand-held thermometer. The quality of the bench top protocol is verified by analyzing Tris buffer certified reference material from Dickson's Scripps laboratory (pH_{ref}=8.093 at 25.0 °C): pH bench-top measurements are consistently within 0.001-0.004 pH units from the certified value. Bench-top pH measurements are referred to as reference pH.



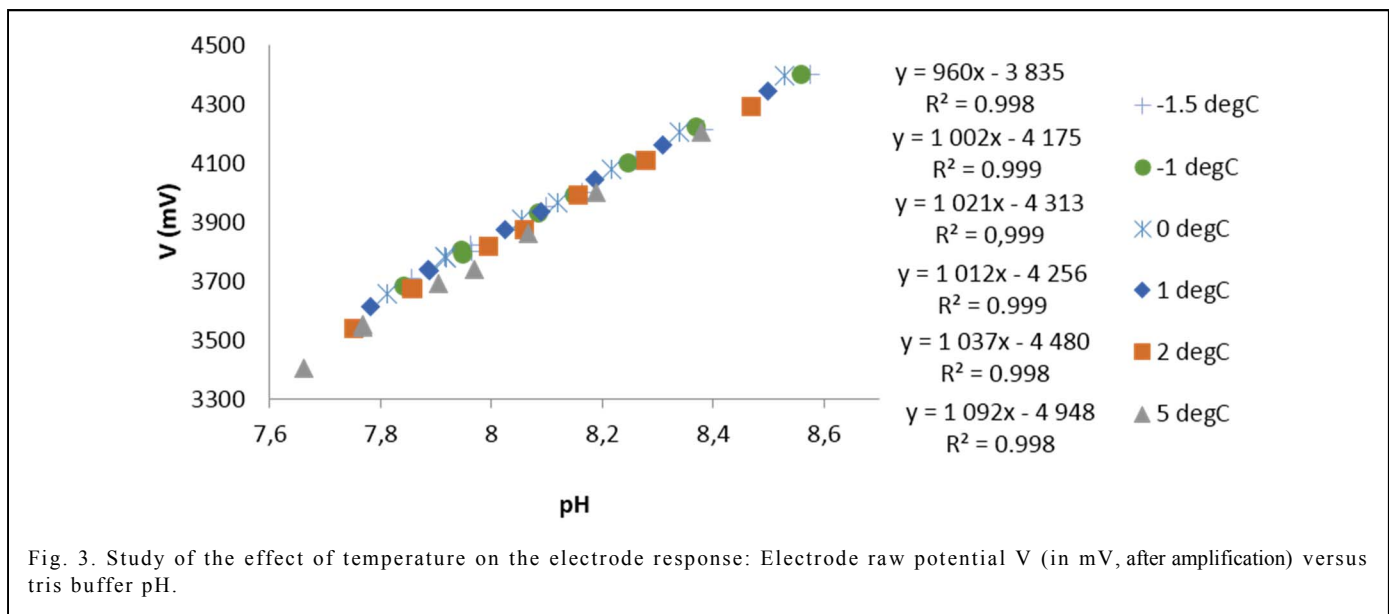


Fig. 3. Study of the effect of temperature on the electrode response: Electrode raw potential V (in mV, after amplification) versus tris buffer pH.

2) Dependence on environmental conditions

Extensive temperature, salinity and pressure tests were performed on a standalone version of the electrode prior to integration within the hybrid system, with temperature tests also performed on the Ferry-box hybrid pH system.

Standalone pH electrode (temperature, salinity and pressure)

The effect of temperature on the electrode was characterized by measuring a range of pH buffers at six different temperatures that are representative of deep ocean, or winter surface, temperatures 5°C, 2°C, 1°C, 0°C, -1°C and -1.5 °C.

The effect of salinity on the electrode response was studied by measuring buffers of various salinities at 25 °C. The range of salinity (26.5-36.5 PSU) was obtained by diluting a single buffer solution of salinity 33.2 with milli-Q water or by adding a few milligrams of NaCl. Resulting solution salinities were measured with a conductivity probe.

Pressure tests were performed by placing the electrode in a custom hyperbaric pressure chamber and repeatedly cycling the pressure in 40-Bar steps, between 20, 60 and 100 Bar. Temperature of the Tris solution inside the pressure chamber was continuously recorded using a temperature logger. The theoretical effect of pressure on the pH of the buffer solution was estimated using equations described in [17].

Ferry-box hybrid pH system (temperature)

To test the performances of the hybrid system at different temperatures, the system was long-term tested with a large batch of Tris buffer at several temperatures between 8°C and 20°C. Small volumes of buffer solution were sampled at each temperature to measure its exact pH value using the bench-top SOP described above.

3) Hybrid pH system calibration

The Ferry-box hybrid pH sensor was calibrated in the laboratory at 20-21°C with large batches of Tris buffers, precisely characterized using the bench-top SOP described above. Water from a reservoir containing sample seawater or different standard solutions was pumped continuously in a loop using a centrifugal magnetic pump. The ambient temperature inside the experimental chamber was controlled through a forced advection air-water heat exchanger connected to a thermostated bath, whereas reservoir temperatures were directly controlled by the bath to accelerate the thermal exchange. Analyzer pH values were obtained from absorbance measurements performed in the MEMS optical cell by using published mCP characterization coefficients from [16]. A slight system-specific linear correction was calculated and applied to compensate for small departures from ideal behavior due to e.g., emission and absorbance bandwidths and/or system geometries [18]. The analyzer measurements were used to calibrate the electrode within the flow-through chamber.

For buoy deployment the colorimetric analyzer was calibrated using Tris buffer as for the ferry-box set up, and its measurements were again used to calibrate the electrode. The difference from the Ferry-box setup was that the electrode was now placed directly in a large seawater bath, whose pH was adjusted in steps by addition of 1M HCl or, respectively, 1M NaOH solutions. Temperature was controlled with a thermostated water bath and chamber.

III. RESULTS

A. Dependence on environmental conditions

Standalone pH electrode characterization

Effect of low temperature on the electrode's calibration is graphically shown in Fig. 3, along with the linear calibration equations obtained at different temperatures. In order to

generate a universal calibration curve, the intercept and slopes of the calibration equations were modeled to first degree as linearly dependent on temperature:

$$pH(V,T)=(a_1*T+b_1)*V+(a_2*T+b_2) \quad (1)$$

where V is the electrode voltage (after signal amplification) and T is the temperature. The linear coefficients a_1 , a_2 , b_1 and b_2 are obtained by regression using the calibration equations from Fig. 3. This universal calibration results in residuals of 0.010 ± 0.009 pH units, which can be considered acceptable given that the most precise reference material available is certified to 0.003 pH units.

The electrode's response is found to slightly decrease with salinity: applying a salinity correction similar to [19] results in a difference of only 0.003 ± 0.006 pH units. The effect of salinity is therefore considered negligible over the 26.5-36.5 PSU salinity range.

Effect of the pressure cycles (in 40 Bar steps) on the electrode's response is presented on Fig. 4. The change of pressure affects the final pH value through two different mechanisms [17]. On one hand, from thermodynamic considerations, a pressure increase of 40 Bar results in a Tris buffer temperature increase in the pressure cell of approximately 0.08°C , which then translates into a pH decrease of about 0.0025 units. On the other

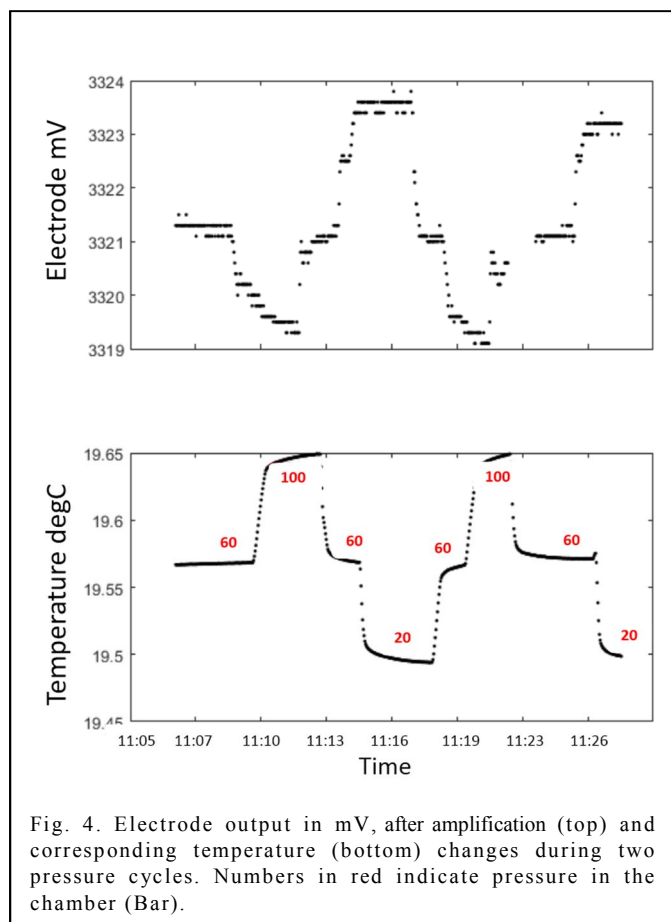


Fig. 4. Electrode output in mV, after amplification (top) and corresponding temperature (bottom) changes during two pressure cycles. Numbers in red indicate pressure in the chamber (Bar).

hand, an increase in pressure results in a separate direct increase in the pH of the Tris buffer solution. Finally, when combining the opposite temperature and pressure effects, the resulting pH of the Tris solution in the chamber increases by only 0.0013 pH units per 40 Bars of pressure increase. The electrode's response changed by 2.2 ± 0.9 mV per 40 Bars step, which corresponds to a relatively stable pH of 7.5060 ± 0.0007 units throughout the pressure cycles after compensating for the temperature change using (1). The pH value measured by the electrode, compared to the actual pH of the Tris subjected to the resulting temperature and pressure changes, resulted in an error of 0.0017 ± 0.0005 pH units per 40 Bars step. This effect of pressure on the electrode's response could be taken into account by applying a linear correction. However, in the following we considered it to be within the measurements error.

Ferry-box hybrid pH system characterization

The results of the colorimetric analyzer at different temperatures compare well to reference measurement with residuals between -0.004 and 0.006, whereas electrode results show a much larger discrepancy at low temperature (residuals up to 0.039) (Fig. 5). The good performance of the colorimetric analyzer demonstrates that the use of the temperature characterization from [16] for m-CP is working well for the temperature range between 8 and 20°C used in this study. For lower temperatures, characterization from [20] should be used. The poorer relative performance of the electrode, on the other hand, seems to be due to instabilities and drift inherent to the hardware and highlights the importance of wisely selecting the frequency of the in-situ corrections using the colorimetric sensor.

B. Hybrid pH system calibration

The hybrid instrument (colorimetric analyzer and electrode) was calibrated in Tris buffer at 21°C , using the procedure explained in the *Instruments and Methods* section. The corresponding graphs are shown in Fig. 6 below. The stability of the colorimetric analyzer's calibration against reagent refilling was confirmed by using a new batch of 2mM mCP

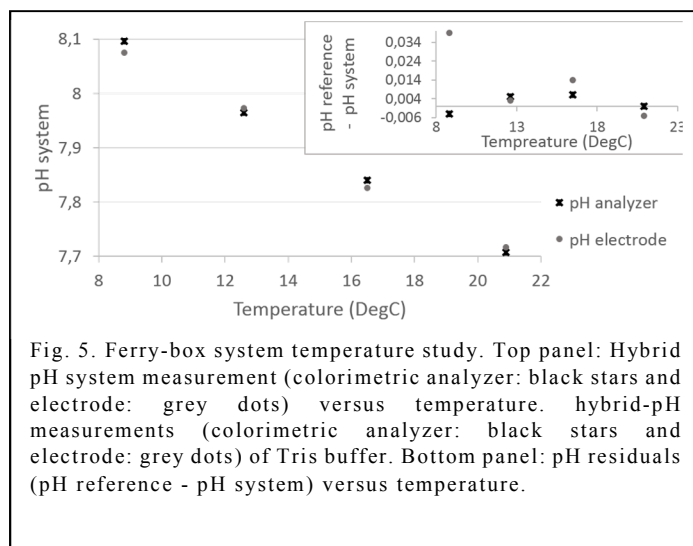


Fig. 5. Ferry-box system temperature study. Top panel: Hybrid pH system measurement (colorimetric analyzer: black stars and electrode: grey dots) versus temperature. hybrid-pH measurements (colorimetric analyzer: black stars and electrode: grey dots) of Tris buffer. Bottom panel: pH residuals (pH reference - pH system) versus temperature.

indicator, prepared a week after the instrument's calibration, and checking the colorimetric analyzer's measurements on two Tris buffer solutions and one seawater sample: the resulting data was within 0.01 pH units from the reference measurement, showing that the calibration of the analyzer was stable and suitable for analysis of both Tris and seawater samples.

A comparison between the pH electrode and the analyzer was then performed in a large seawater volume at 21 °C. The pH of the seawater was adjusted in multiple steps by successively adding 0.1 M HCl and 0.1 M NaOH solutions. Electrode and analyzer datasets followed the same general pattern but an offset of 0.2 pH units was observed between the two curves (Fig. 7), with the pH electrode reading higher than the colorimetric analyzer. Reasons for such a large offset are not clear but are probably due to the nature of the media, possibly compounded with electromagnetic interferences from other laboratory instruments (e.g. water bath or pump). To compensate for this offset, the electrode was re-calibrated directly using the colorimetric analyzer's seawater data (Fig. 6, bottom), which completely removed the initial offset (Fig. 7). An important conclusion can be drawn from this observation: to avoid any type of media effects, the electrode should be calibrated directly in seawater using parallel measurements from the colorimetric analyzer, or, as a minimum, at least one reference point should be used to re-adjust the electrode to correct for interferences.

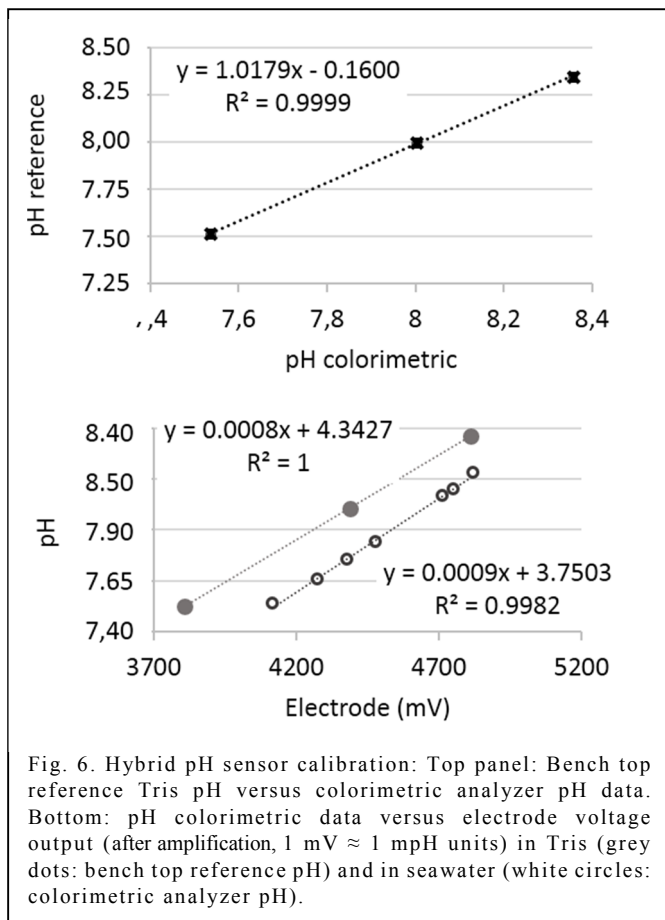


Fig. 6. Hybrid pH sensor calibration: Top panel: Bench top reference Tris pH versus colorimetric analyzer pH data. Bottom: pH colorimetric data versus electrode voltage output (after amplification, 1 mV \approx 1 mpH units) in Tris (grey dots: bench top reference pH) and in seawater (white circles: colorimetric analyzer pH).

C. Buoy deployment data

Colorimetric analyzer data during the buoy deployment are shown in Fig. 8. No usable electrode pH data were obtained due a cable waterproofing issue, which has since been fixed. The colorimetric analyzer worked well during the one-week deployment at a measurement frequency of two measurements per hour. Fig 8 also shows the moving average (overlay) and moving standard deviation (bottom) obtained over a window of 12 data points (6 hours). The data demonstrates good stability, with main variations likely due to natural variability (e.g. tides). The system precision is about 0.002 pH units as observed in the plateau-like part of the dataset on the 15th of January.

IV. CONCLUSIONS AND FUTURE WORK

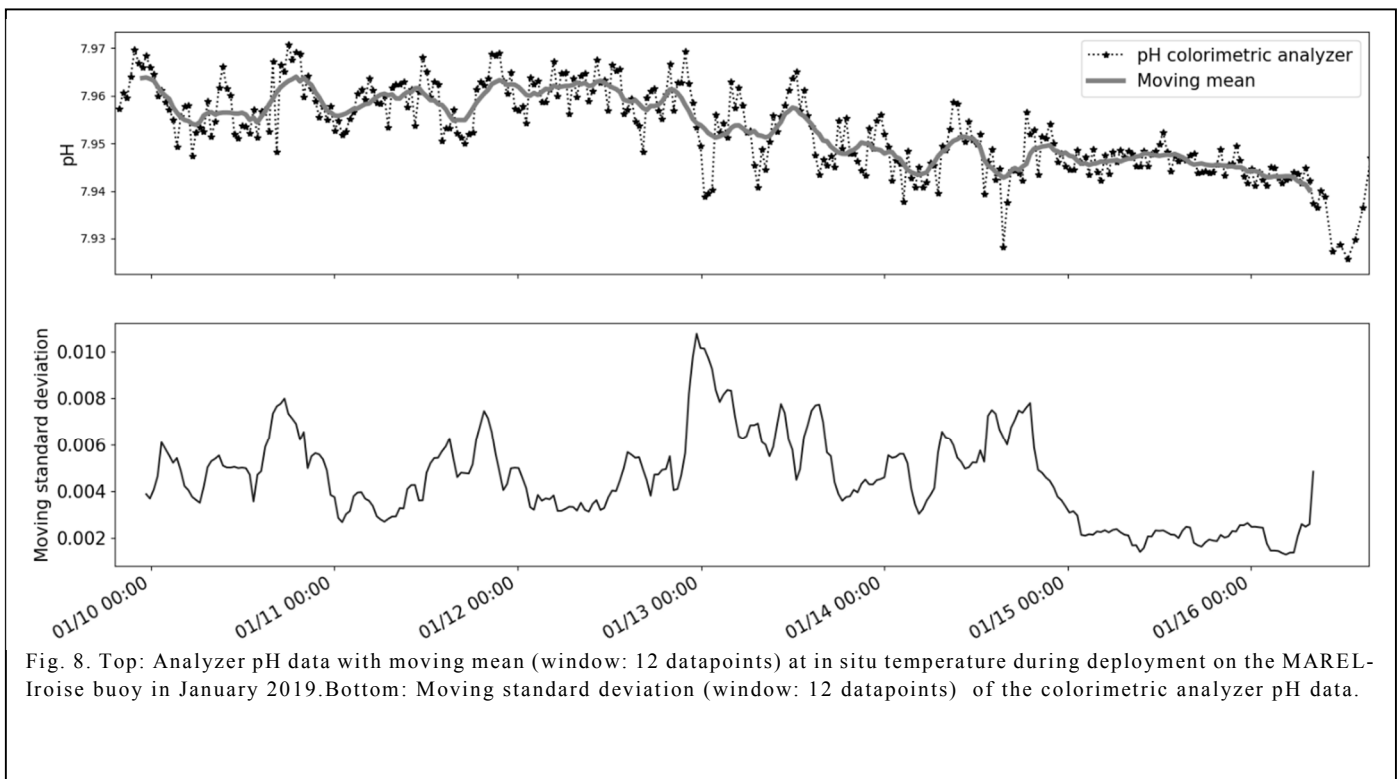
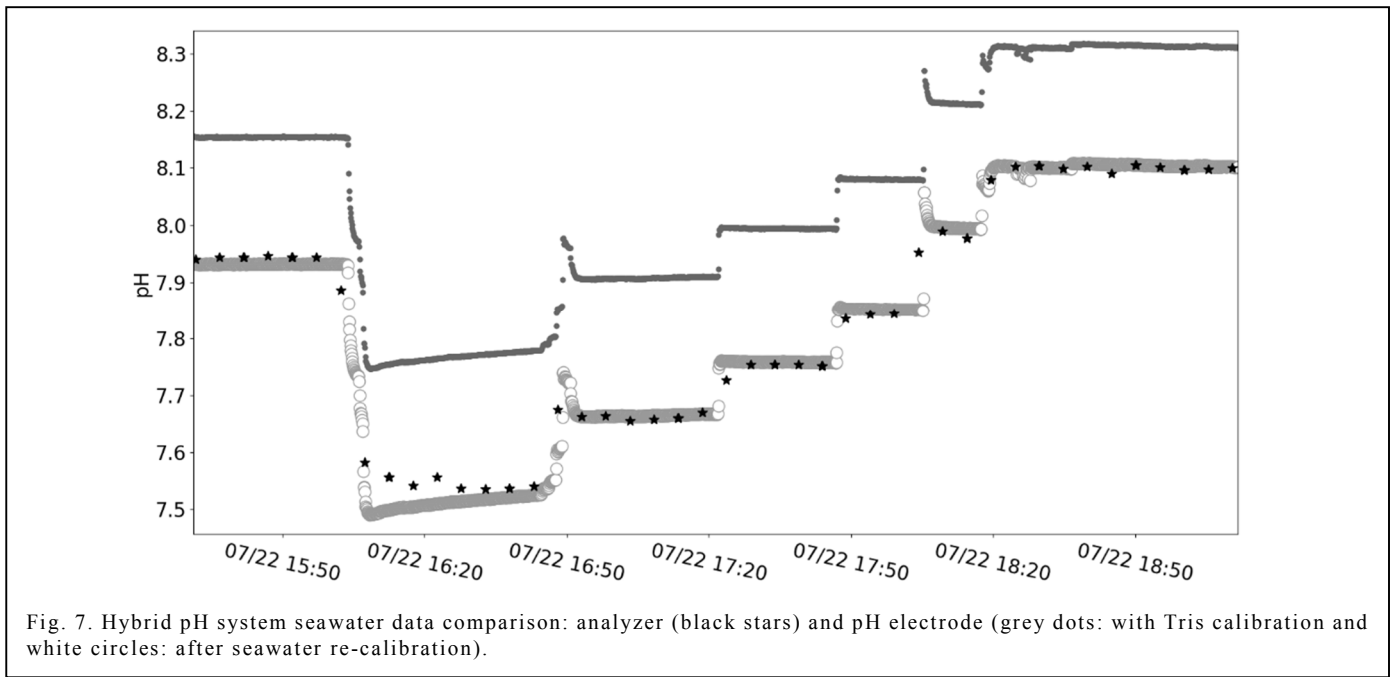
Results show that the potentiometric part of the hybrid sensor is capable to operate in real ocean pressure and temperature conditions. The electrode can perform well in near-freezing temperatures and appears suitable for Arctic environmental conditions. The colorimetric part of the hybrid sensor provides a stable reference to perform periodic recalibrations and remove drift. Protocols to calibrate both colorimetric and potentiometric sensors have been improved with an initial characterization of the colorimetric analyzer performed in Tris buffers, and a subsequent characterization of the electrode performed in seawater using the colorimetric analyzer as reference. While data from short-term buoy deployment look very encouraging, additional system characterization with multiple pH and temperature steps is needed to achieve target data quality (0.010 pH units accuracy, 0.001 pH units precision). The next deployment of the hybrid system in a seawater tank facility will be used to study the colorimetric analyzer sampling frequency required to re-calibrate the electrode's data. In parallel, adaptation of the colorimetric analyzer housing for in-situ deployments at depth has started.

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Collaborators' affiliations:

3. UEM-UBO, UMS CNRS 3113, Technopôle Brest-Iroise, Place Copernic, F-29280 Plouzané, France, Peggy.Rimmelinmaury@univ-brest.fr.



4. Ifremer-Centre de Brest, REM / RDT / DCM, Z.I. de la Pointe du Diable, CS 10070, 29280 Plouzané, France, Loic.Quemener@ifremer.fr, Michel.Repecaud@ifremer.fr.
 5. Station Biologique de Roscoff, UPMC, UMR CNRS 7144, pl. Georges Teissier, CS90074, 29688, Roscoff, France, bozec@sb-roscoff.fr.
 6. CNRS/INSU, Division Technique, 1 place Aristide Briand, 92195 Meudon, France. laurence.beaumont@cnrs.fr, antoine.guillot@cnrs.fr.

COAST-HF website: <https://www.ir-ilico.fr/Les-reseaux-elementaires/Fiches-d-identite-des-reseaux-elementaires/COAST-HF> (INSU-CNRS-IFREMER-IUEM/UBO)
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