pH Sensor Calibration Procedure

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Abstract—This paper describes the calibration of pH sensor located at the OBSEA marine observatory. This instrument is based on an industrial pH electrode that is connected to a CTD instrument (Conductivity, Temperature, and Depth). The calibration of the pH sensor has been done using a high precision spectrophotometer pH meter from Institute of Marine Sciences (ICM), and in this way it has been obtained a numerical function for the pH sensor proportional to real pH.

I. Introduction

The pH is a way to quantify how much acidic or basic (alkaline) is a solution [1-2]. To identify changes in the seawater, a pH sensor has been developed to operate in the OBSEA underwater observatory [3]. The instrument is based on an industrial pH electrode of Honeywell [4-6] that is connected to a CTD instrument. The pH electrode is a non-glass electrode that resists breakage in normal usage and offers up to 10 times faster responses than glass [7]. The ISFET-based, solid state pH electrode emits a stable, low impedance signal, eliminating the need for frequent calibrations.

The calibration of the pH sensor located at the OBSEA has been done in two phases. In the first phase it has been calibrated the temperature value provided by the sensor. The second phase consists in the calibration of pH provided by the sensor comparing this with the spectrophotometer from the Institute of Marine Sciences (ICM) [8].

II. Detailed Description

The pH electrode provides one analog output voltage proportional to the measured pH and one analog output resistance proportional to the temperature. The electrode signals cannot be connected directly with the CTD instrument; due to this it has been designed a signal conditioning [9]. These two signals are connected to the analog inputs of the CTD instrument. The measuring system of the pH sensor proposed for the OBSEA observatory is shown in Figure **1**.
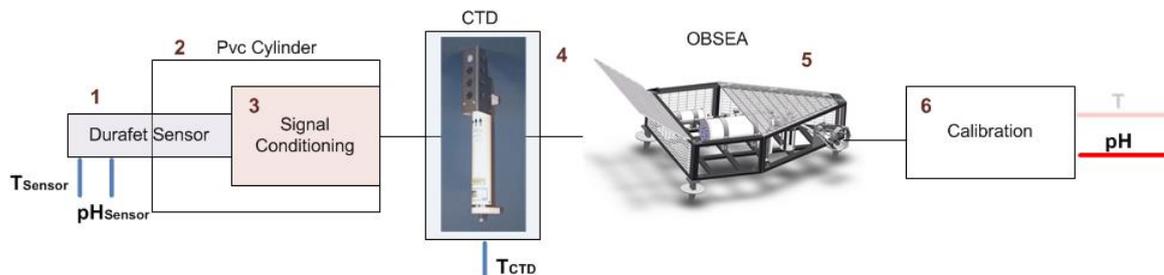

Figure 1 Measurement System

The measurement system comprises the following components:
1. PH Sensor Honeywell Durafet 07777DVP.
2. PVC Watertight Cylinder of 75mm diameter.
3. Electronics for sensor signal conditioning of PH.
4. CTD that measures the output signals of the pH sensor.
5. OBSEA observatory
6. Data acquisition system, where received data from the pH sensor is processed accordingly to the numerical function found in the calibration process.

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III. Calibration System

To obtain the pH value there have been used two procedures. In the first procedure the temperature value is calibrated. In the second procedure the pH value is calibrated. These calibration values are used to obtain the final numerical pH value.
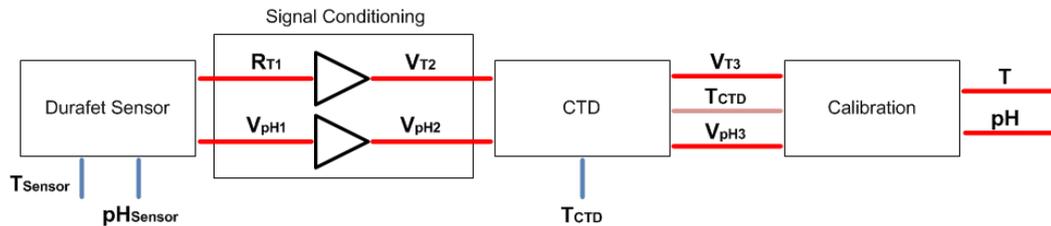Figure 2 shows a more detailed description of the measuring system.

Figure 2 Description of the measurement system

- R_{T1}: Durafet output temperature sensor. Resistance proportional to the temperature. Order of $K\Omega$.
- V_{T2}: Analog output voltage signal. Voltage proportional to the temperature. Order of V.
- V_{T3}: Analog voltage measured provided by the CTD. It is the same voltage that V_{T2}.
- T: Temperature value in °C.
- V_{pH1}: Durafet output voltage sensor. Voltage proportional to pH. Order to mV.
- V_{pH2}: Analog output voltage signals. Voltage proportional to pH. Order to V.
- T_{CTD}: Temperature measured by the CTD sensor in °C.
- V_{pH3}: Analog voltage measured provided by the CTD. It is the same voltage that V_{pH2}.
- pH: pH value.

A. Temperature calibration procedure

To calibrate the temperature, the measurement system (Figure **2**) is introduced in a climatic chamber with different temperatures. During this period, the output data from the temperature sensor is acquired and stored for further processing.

Values were compared using two methods. In the first method the value of temperature T was obtained in relation to voltage V_{T3}. In the second method the value of temperature T was obtainde in relation to voltage V_{T3} taking into account the conditioning circuit parameters (constants of the thermistor).
Referencing the temperature provided by the CTD sensor in the Figure 3 shows that the first method has an error 0.23 ° C while the second method an error is 0.053 ° C.
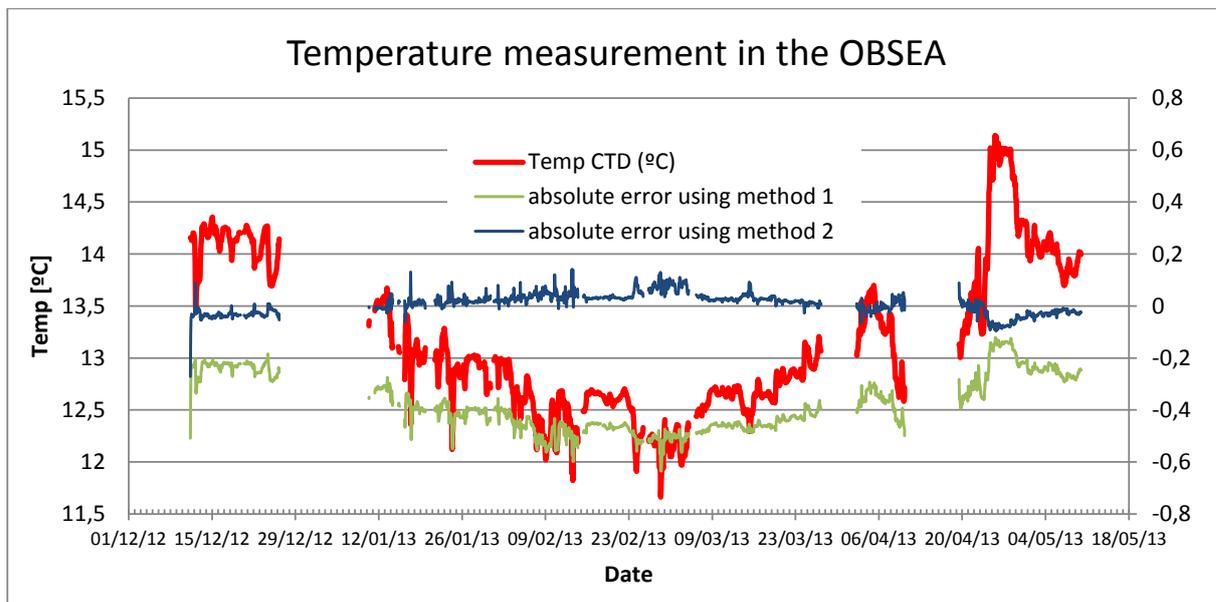
Figure 3 Comparison of values temperature between two methods of calibration

B. pH calibration procedure

To calibrate the pH are used the V_{pH1} and V_{pH3} output values of measurement system (Figure 2). First, the sensor was calibrated using buffer solutions of pH. Secondly, the sensor has been recalibrated using water samples from OBSEA Observatory which was measured with a spectrophotometer from ICM institute.

Steps taken during the calibration procedure:

1) Get the relationship between V_{pH1} (V1) and V_{pH3}.

2) Get the sensor calibration factors
   - pHs = pH calibration substance
   - Ts = temperature of the calibration substance (in K)
   - $V0$ = output voltage of the sensor for calibration substance

3) Calculation of the parameter $E0$ after calibration

$$E0 = V0 - pHs * R * Ts * \ln(10)/F. \qquad (1)$$

Where R (Universal Gas Constant) and F (Faraday Constant) values $R= 8.31451kPa$ and $F = 96487\ C/mol$

4) Calculation of final pH

$$pH = F*(V1 - E0 + 0.001(Temp - Ts))/(R * (Temp) * \ln(10)) \qquad (2)$$

Where the temperature $Temp$ and Ts must be in Kelvin

The output voltage value from the pH sensor is calculated using equation (3)

$$V1 = -0.064*V_{pH3} + 0.1557 \qquad (3)$$

Table 1 Calibration values for the used standard

pHs	Ts [K]	V0 [mV]

| 7.839 | 293.8215 | 0.0552 |

Using equation (1) and values from the calibration has been obtained ***E0 = -0.401862187.***

Tabl2 2 Calibration values for the OBSEAwater sample

pHs	Ts [K]	V0 [mV]
8.096	286.007	0.073431

With the values obtained in the in situ calibration and using equation (1) the E0 parameter have been recalculated, *E0= -0.38612*

As seen in the figure5, using the calibration parameters obtained in the laboratory, the nominal pH is around 8.3, and using in situ calibration, the pH values is around 8.1. Giving the value of the pH measured with the spectrophotometer of ICM institute of about 8.1, the final calibration parameters obtained from in situ calibration is chosen.
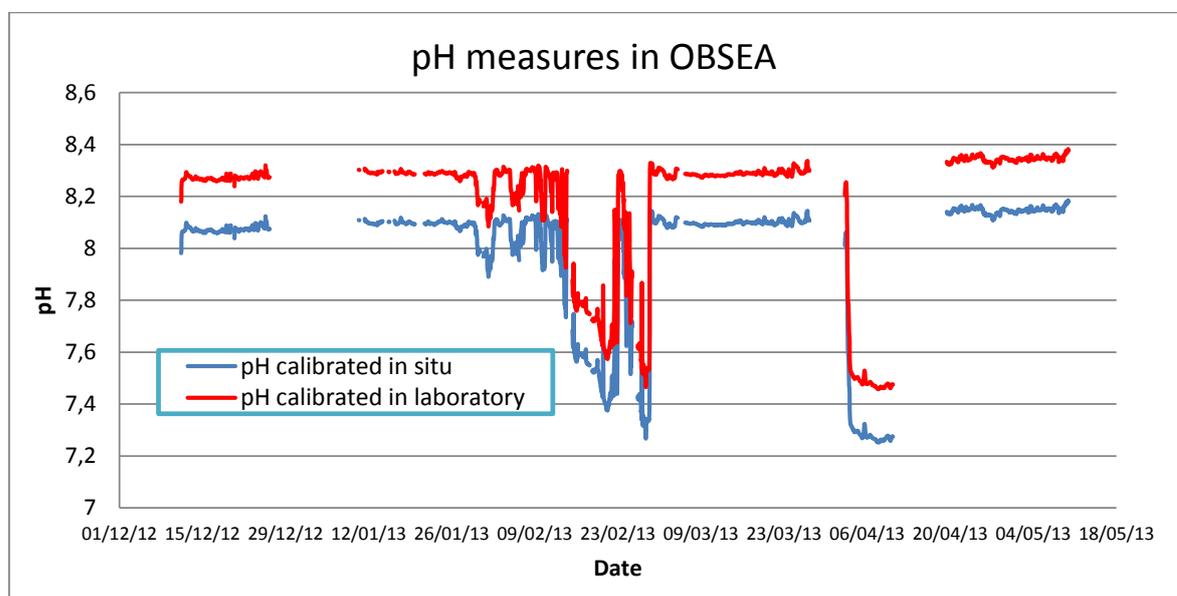

Figure 4 Comparison of values pH between two methods of calibration

IV. Conclusions

A system to measure the pH of the sea water has been designed for the OBSEA observatory. The calibration of the system has been performed and the numerical function for the pH sensor proportional to real pH has been obtained. The pH sensor has been installed in the observatory and the data has been collected for five mouths which demonstrate that the system works properly with an accuracy of 0.1. In order to achieve the desired accuracy in situ calibration has been fundamental.

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