ANB Sensors

Calibration-free pH sensor : A Case Study

December 2021

creating a more sustainable planet by advancing environmental sensors

ANB Sensors

4 Penn Farm, Haslingfield, Cambridge, CB23 1JZ, UK
Registration number: GB 9526512

Table of Contents

ANB Sensors

4 Penn Farm, Haslingfield, Cambridge, CB23 1JZ, UK
Registration number: GB 9526512

1. Introduction

Since the beginning of the industrial revolution the ocean has become increasingly more acidic due to uptake of atmospheric CO_2. It is evident there is an urgent need for in situ pH measurements to provide high spatial and temporal resolution. However, todays ship-based and tethered-mooring measurements cannot achieve this, and whilst the introduction of intelligent and low-cost Underwater vehicles (UVs) provide the platform to obtain the data, the development of small, fast, low power, and reliable pH sensors for deployment on these smaller AUVs is lagging behind.

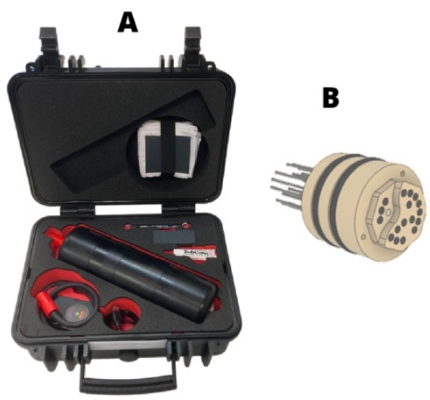
2. Current Technology

Today's ocean pH sensors include optical sensors that use a dye that changes colour in different pH test fluids, an ISFET system where the current through a semiconductor device changes when hydrogen ions are present in the test fluid, and finally the standard glass electrode technology placed in a suitable housing. The colorimetric systems whilst being very accurate, are generally large and expensive, require replacement dye bags and have a long measurement times (ca. 5mins). Such technology does not obtain the required measurement frequency for fast moving UV. The ISFET technology whilst producing a high measurement frequency, requires annual recalibrations and specific corrections for depth and salinity. The glass electrode is not very robust, has to be kept in a storage solution when not in use, and requires frequent recalibration due to reference electrode drift.

3. ANB Sensors Technology

pH is one of the key ocean variables and for too long the pH sensor has been the 'problem child' of the sensor suite. At ANB Sensors we set about the task of developing a pH sensor that would get around all the drawbacks of the current available technologies, namely; calibration-free, robust, small, no storage issues, and to be easy to use and maintain.

The S Series pH sensors are based on patented electrochemical technology to provide a calibration free sensor. The biggest reason why electrochemical based pH sensors require frequent recalibrations is reference electrode drift – where the reference to which the pH is measured against is not stable and moves with time, making the measurement inaccurate until the sensor is recalibrated. ANB's technology contains an innovative reference tracker, which follows any drift in the reference and accounts for it in-situ, removing the need to manually recalibrate. The S Series, shown as (A) in the figure, is made from robust materials, is all solid-state, so ideally suited for the extreme environments found in the world's oceans.

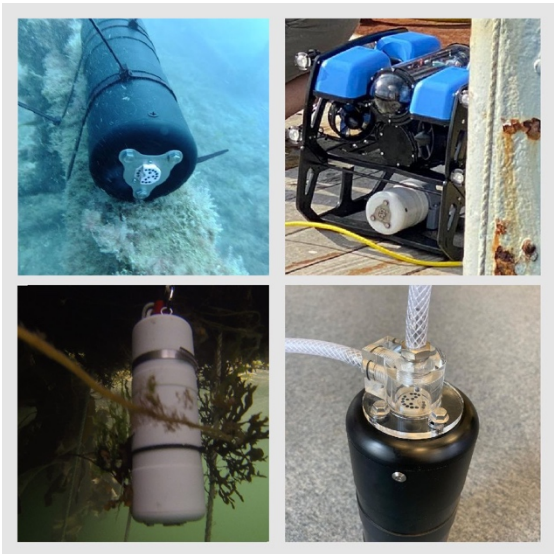


The key element of the S Series is it sensing transducer (B). This is where ANB's innovative sensing chemistry is found. It contains a series of solid-state carbon impregnated electrodes from which the electrochemical measurements are conducted. The sensors on-board computer analyses the electrochemical measurement the temperature of the solution and combines these factors and produces the outputted pH to the end user. There is no need to compensate for depth with the sensor providing outputs of time, pH, temperature and health.

The output of health is key to the end user experience as it provides a qualifier on the accuracy of the pH response and if maintenance of the sensor is required. The lifetime of the sensor is dependent on the number of measurements that each electrode records and not on the deployment time of the sensor. The sensor has an on-board processor which assesses the response of each electrode after every measurement. The data is passed through unique algorithms onboard the sensor which provide the end user with real time health and performance information on their sensor and will give an alert when maintenance is required. Maintenance is a simple abrasion over the surface of the transducer, with the supplied abrasion block. This process merely replenishes the transducer interface and, after abrasion is carried out, the sensor is ready for deployment, with no recalibration necessary.

The lifetime of the transducer is dependent on the number of measurements the sensor records, so therefore depends on the measurement profile set by the end user. The transducer provides approximately 15,000 measurements before maintenance is required, so, on a continuous measurement profile will last for ~5 days, or on a 15-minute measurement interval profile, will last for ~50 days before it requires an abrasion. The transducer survives for 25-30 abrasions before a replacement is required. Replacing the transducer is a very simple process that the end user does themselves and, once a new transducer is installed the sensor is ready to start measuring, no calibration is required.

The sensor is responds instantly to the pH of the solution in which it is immersed. The nature of the measurement that is recorded at each electrode on the transducers surface means that the S Series current maximum measurement rate is ca.23s. The challenge to lower this measurement frequency for fast moving vehicles is being taken on at ANB with concepts and processes already being worked up at ANB laboratories. This is conjunction with stretching the salinity range in which the sensor operates. The S Series operates across the range 10-37ppt taking allowing the higher end of brackish water salinities to full ocean salinities to be monitored without compensation and maintaining the accuracy specifications of the sensor. ANB are now developing their full salinity sensor conducting their first river water trials.



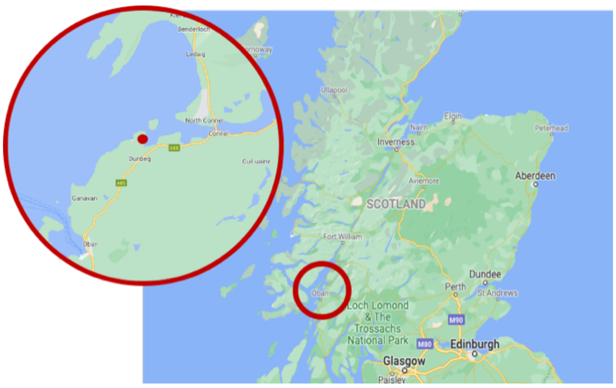
The S Series have been designed so they are mechanically robust, can be stored wet or dry and require minimal user intervention. Another important feature is that the technology is accessible for all the different platforms, namely buoys, vehicles, floats and sondes. The S Series sensors come in a range of depth ratings and sizes, including an un-housed version for tighter integration into vehicles.

ANB Sensors

4 Penn Farm, Haslingfield, Cambridge, CB23 1JZ, UK
Registration number: GB 9526512

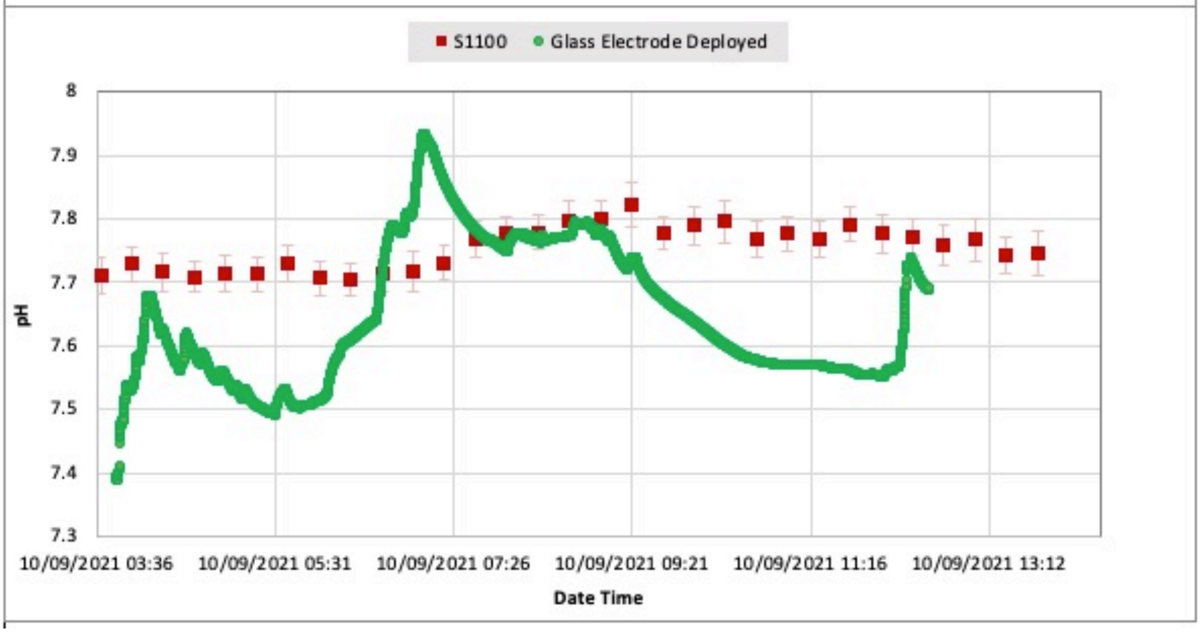
4. Field Trials

Multiple sensor field trials have been conducted by ANB Sensors including on a ferry box travelling between Stockholm, Sweden and Helsinki, Finland measuring in the brackish water found there, integrated on a remotely operated vehicle in California, USA, on a mooring in Southampton, UK and the Cam river in Cambridgeshire, UK. In all of these trials it has been ANB Sensors aim to improve and optimise the sensors. The S1100 uses a digital output making it easier to integrated into today's UV's control systems and can be configured to provide the desired output to the end user. Its sleek design means it can be tethered to an ROV or should the end user wish for a tighter integration the OEM kit is available. This allows for the sensors electronics to be housed inside the vehicle and the transducer sealed in the vehicles walls using its double o-ring design. Flowloop integration for ferrybox and sample lines is achieved by placing a flowcup on the front face of the sensor. Finally, the sensor can just as easily be tethered to a rope or mooring for open ocean profiling and buoy surveys. The data and end user experience that has been collected from these deployment conditions has driven the development of the sensor to it current technical specifications and end user experiences.



Field trials of the S1100 pH sensor were carried out at the Scottish Association for Marine Science (SAMS) campus near the village of Dunbeg, 3.5 miles north-east of Oban on the west coast of Scotland.
The sensors were deployed from the static research vessel that is stationed on a pontoon adjacent to the SAMS campus. The sensor was positioned at approximately 2m depth and connected to a battery at the surface via a SubConn cable. Water samples were taken alongside the sensor so the pH could be independently measured back in the laboratory. Also, an oceanographic glass pH electrode was deployed over the same timescales for a direct comparison.

The plot, shown as the top figure, is the data output from the sensor after 36 hours of measuring on a 15-minute measurement interval. The bi-daily variations in pH ranging from pH 7.7 up pH 7.9, consistent with the natural ebb and flow of the tidal waterways at Oban, can clearly be observed. At high tide the river water is mixed with the incoming sea water producing a higher pH value than the natural source waters. The data was corroborated by sampling taken during the course of the trials, whereby the pH was measured using a freshly calibrated glass electrode.



During the course of the trials an oceanographic glass-based pH sensor was tested alongside the S Series sensor. This data is shown in the bottom figure. The glass electrode data shows a wide variation in pH during the course of its deployment which did not follow the tidal variations highlighted by the ANB Sensors technology.

These trails show the efficacy of the sensor compared to the competition, however, they are not the end as ANB sensor demonstrates its utility so sense pH in some of the harshest monitoring conditions for today's sensors. Through European Union funded Jericho –S3 grants two sensors are currently deployed off the coast of Barcelona with UPC. This area in the Mediterranean is known for its prevalent biofouling. In the coming weeks two further sensors will be sent to HCMR, Greece. These are interesting given the higher temperature and salinity conditions observed compared to bulk ocean conditions, causing today's sensors to fail and drift as they are outside of their workable ranges.

5. Conclusions

The S1100 has been designed with the end-user in mind to minimise the pain of monitoring pH. In designing and producing the S1100 ANB have engaged with end users and integrators to understand their pain points. Overwhelmingly calibration, storage conditions and deployment difficulties were found as the key issues. The calibration free, solid state, plug and play nature of the S1100 ensures that end user pain points are removed. The S1100 has been demonstrated under a number of deployment conditions ferrybox, Buoy, open ocean and shown to provide accurate pH measurements compared to its today's sensors.

6. Acknowledgements

The authors would like to acknowledge the excellent team of scientists and engineers at ANB Sensors: Christina Day, James Dyer, Ben Legg, Brett McElwaine, Brandon McHale, Monica Miranda Mugica, Richard Seymour and Neel Sisodia along with the support staff: Carl Clemans, Chris Copping and Vicki Georgiadis. Furthermore we are grateful for the guidance of Gareth Lee and Daisy Pickup from the University of East Anglia.