DATA PRODUCT SPECIFICATION
FOR PH OF SEAWATER

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in Cooperation with

University of California, San Diego
University of Washington
Woods Hole Oceanographic Institution
Oregon State University
Scripps Institution of Oceanography
Rutgers University
### Document Control Sheet

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Data Product Specification for pH of Seawater

Signature Page

This document has been reviewed and approved for release to Configuration Management.

OOI Senior Systems Engineer: [Signature]

Date: 2012-08-20

This document has been reviewed and meets the needs of the OOI Cyberinfrastructure for the purpose of coding and implementation.

OOI CI Signing Authority: [Signature]

Date: 2012-08-20
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Abstract
This document describes the computation used to calculate the OOI Level 1 pH of seawater core data product, which is calculated using data from the Sunburst SAMI-II pH instrument (PHSEN). This document is intended to be used by OOI programmers to construct appropriate processes to create the OOI Level 1 pH of seawater core data product.

Introduction

2.1 Author Contact Information
Please contact Merrie Beth Neely (mneely@oceanleadership.org) for more information, or the Data Product Specification lead (DPS@lists.oceanobservatories.org).

2.2 Metadata Information

2.2.1 Data Product Name
The OOI Core Data Product Name for this product is
- PHWATER

The OOI Core Data Product Descriptive Name for this product is
- pH of seawater

2.2.2 Data Product Abstract (for Metadata)
The OOI Level1 pH of seawater core data product is a measure of the acidity or basicity of a seawater sample on the total hydrogen ion scale (pH\textsubscript{T}) used for CO\textsubscript{2} system calculations, nominally the concentration of hydrogen ions in seawater. However, pH is not precisely the concentration of hydrogen ions, but takes into account an activity factor. Hydrogen ion activity coefficients cannot be measured directly by any thermodynamically sound method, so they are based on theoretical calculations. The pH scale is defined in practice as traceable to a set of standard solutions whose pH is established by international agreement, but in the case of the Sunburst Sensor instrument and the measurement of seawater pH, Andrew Dickson’s Tris CRMs are used to verify the accuracy before and after deployment; thus, the SAMI-pH measurements are directly traceable to the Dickson CRMs. The Tris CRM standards are accurate to \(\pm0.002\) pH units, but are only available at a single pH value and therefore validation over the entire pH operating range is not possible. The pH of seawater plays an important role in the ocean’s carbon cycle. Ocean acidification caused by carbon dioxide emissions, can affect oceanic flora and fauna in many ways as well as biochemical and geochemical reactions.

2.2.3 Computation Name
Not required for data products.

2.2.4 Computation Abstract (for Metadata)
This computation computes the OOI Level 1 PH of seawater core data product, using data from the Sunburst SAMI-II pH instrument (PHSEN).

2.2.5 Instrument-Specific Metadata
See Section 4.4 for instrument-specific metadata fields that must be part of the output data.

2.2.6 Data Product Synonyms
Synonyms for this data product are
- pH of water
- pH
2.2.7 Similar Data Products

There are no similar data products. However, $pCO_2$ measurements are related to pH in that both are used to describe the carbon chemistry of sea water.

2.3 Instruments

The Sunburst SAMI-II pH instrument was selected by the OOI to make this measurement on both mobile and fixed platforms. The instrument will have a copper intake tube to limit biofouling. On-board reagents and standards must be loaded prior to each deployment and must be within the manufacturer’s expiration date (shelf-life) for proper operation. For information on the instrument from which the inputs to OOI Level 1 pH of seawater core data product are obtained, see the PHSEN Processing Flow document (DCN 1342-00510). This document contains information on the PHSEN instrument class make/model; it also describes the flow of data from the PHSEN instruments through all of the relevant QC, calibration, and data product computations and procedures.

Please see the Instrument Application in the SAF for specifics of instrument locations and platforms. This instrument will not be used on gliders or AUV’s, but will be used on the RSN surface-piercing profiler/shallow profiler.

2.4 Literature and Reference Documents


OPERATING MANUAL AFT/SAMI$^2$-pH, Sunburst Sensors LLC, (Version unknown but circa February 2012)


See also anything posted on:
https://confluence.oceanobservatories.org/display/science/Common+Instrument+ICD
https://confluence.oceanobservatories.org/display/Presentations/OOI+PHSEN+Collaboration
2.5 Terminology

2.5.1 Definitions
The following terms are defined here for use throughout this document. Definitions of general OOI terminology are contained in the Level 2 Reference Module in the OOI requirements database (DOORS).

Concentration - is a measure of the amount of something in something else, in this case the amount of hydrogen ions per kg of solution.

2.5.2 Acronyms, Abbreviations and Notations
General OOI acronyms, abbreviations and notations are contained in the Level 2 Reference Module in the OOI requirements database (DOORS). The following acronyms and abbreviations are defined here for use throughout this document.

COTS – commercial off the shelf
DI – Deionized water
mCP - meta-Cresol Purple
LED – light emitting diode
TB - thymol blue
Tris – tris(hydroxymethyl)aminomethane, with the formula (HOCH₂)₃CNH₂
SAMI = Submersible Autonomous Moored Instrument, specifically the Sunburst AFT/SAMI-II-pH

2.5.3 Variables and Symbols
The following variables and symbols are defined here for use throughout this document.

ε - molar absorptivities
K’a – dissociation constant
pK’a – negative log of the dissociation constant
e₁, e₂ and e₃ – salinity and temperature-dependent ratios of the molar absorptivities (ε) of Hl⁺ and I₀ at 434 and 578 nm determined at the factory and provided by the vendor in the firmware
R - absorbance ratio A578/A434
I – a measure of the light intensity transmitted through a seawater and indicator mixture
I₀ – a measure of the light intensity transmitted through a pure seawater solution (blank)
A – absorbance at each wavelength

3 Theory

3.1 Description
The Sunburst Sensor Sami II pH instrument allows the user to measure seawater pH on the total scale (pHₜ) using a colorimetric reaction occurring in an indicator solution. A seawater sample stream is pumped through the instrument and injected with a pH-dependent indicator solution. Two wavelength-specific LEDs send alternating pulses of light through the indicator-sample mixture as it is pumped through a flow cell. The ratio of the absorbance at the two wavelengths with and without the dye, Beer’s law, and the molar absorptivities of the indicator can be used to calculate the concentration of protonated and un-protonated indicator. The indicator pK’a is then used to calculate pH. pHₜ measures the ratio of indicator dye in a seawater sample and infers the activity of both protons (free hydrogen ions) and hydrogen sulfate ions in the colorimetric reaction. It is the preferred method for evaluating CO₂ measurements in seawater. The alternatives are the free scale (pHₕ), which ignores hydrogen sulfate ions and can only be considered an
estimate, and the seawater scale ($\text{pH}_{\text{sws}}$), which further accounts for protonation interactions between hydrogen and fluoride ions.

**Optical Path**
The SAMI uses pulsed LEDs with narrow band filters at wavelengths corresponding to maximum optical absorbance for the protonated and deprotonated forms of the reagent. A reference photodiode tracks changes in the light sources. Light is transmitted to and from the flow-cell via 800-µm optical fibers. In the SAMI-pH the flow-cell optical path length is 1 cm.

**Fluid Path**
The SAMI-pH uses a 50 µL solenoid pump to drive reagent through the system. A solenoid valve allows the same pump to introduce a single pulse of reagent into the stream for each pH measurement. A 350-µL static mixer upstream of the flow cell ensures thorough mixing of the sample and reagent prior to optical measurements. The sample’s blank signal intensity ($I_0$) is established by taking measurements while pumping pure sample through the flow cell. After measuring the blank signal, reagent is introduced into the flow stream and light intensity ($I$) is collected as the pump pushes the mixture through the flow-cell. Optical blanks are required so that accurate indicator absorbance ratios ($R$) can be calculated.

### 3.2 Mathematical Theory

**Equilibrium Reaction**
Spectrophotometric pH determination is based on the equilibrium reaction of a pH-dependent indicator. A diprotic sulfonephthalein indicator, meta-Cresol Purple (mCP), is used as the reagent. A single 50-µL pulse of reagent is introduced into the seawater stream. The ratio of the acidic ($\text{HI}^+$) and basic ($\text{I}^2-$) forms of the indicator varies based on the pH of the seawater being tested.

Indicator equilibrium is described by Equation 1: \[ H\text{I}^- \rightleftharpoons K_a' I^2- + H^+ \]

where $K'a$ and $pK'a$ are the apparent dissociation constant and the negative logarithm of the apparent dissociation, respectively. The acidic and basic forms of the indicator are measured at peak absorbance wavelengths of 434 nm ($\text{HI}^+$) and 578 nm ($\text{I}^2-$). The diprotic $\text{H}_2\text{I}$ form is not present at seawater pH and therefore is not considered in our applications.

Combining the log form of the indicator equilibrium expression and Beer’s Law results in

Equation 2: \[ \text{pH} = pK'a + \log \left( \frac{(R-e_1)/(e_2-Re_3)}{I/I_0} \right) \]

where $R$ is the absorbance ratio A578/A434, A578 refers to the absorbance at the wavelength 578 nm and A434 refers to the absorbance at the wavelength 434 nm, and the $e_i$ are the salinity and temperature-dependent ratios of the molar absorptivities ($\varepsilon$) of $\text{HI}^+$ and $\text{I}^2-$ at 434 and 578 nm.

The absorbance at each wavelength is calculated as:

Equations 3: \[ A = -\log \left( \frac{I}{I_0} \right) \]

where $I$ is a proportional (not actual) measure of the intensity of light transmitted through a seawater and indicator mixture and $I_0$ is a proportional (not actual) measure of the intensity of light transmitted through pure seawater (the blank).

### 3.3 Known Theoretical Limitations

Algorithm results are only valid between 0 – 35 °C and at 35(+/-1) salinity. The algorithm default assumes a salinity of 35 and does not appreciably affect pH accuracy if salinities are +/- 1, however, when salinities drop below 34 or go above 36, a correction can be applied through data.
post-processing using salinity data from a nearby instrument. Alternatively, if the PHSEN instrument is connected to a SeaBird CTD a subroutine can be programmed into the driver to replace the default of 35 with the most recent salinity value from the CTD in the equation. **The code for this subroutine is available from Sunburst upon request.**

It is known impurities exist in the TB and mCP commercially available today from all vendors. The impurities lead to variations in light absorbance, affecting the calculations of molar absorptivities and thereby pH (Liu et al, 2011, among other authors). This type of error will be minimized through the removal of impurities in new reagent batches and also through algorithm adjustments reflected in future software upgrades, and validated at water sample temperatures down to 5˚C (Liu et al, 2011). Both reagents and software upgrades are planned for release in late 2012, at which time this DPS will need revised. It is also known characteristics of the dye change with pressure, but the effects are not yet well understood. This is currently not accounted for in the calculation of pH presented here.

**Acknowledgment of the State of the pH Sensor by OOI Scientists**

Measurements of oceanic pH on the low end of the range specified in the OOI requirements (7.3 to 8.5) are not uncommon today (1) in the N Pacific Ocean (see Figures 1 and 2, methodologies may differ). The precision of spectrophotometric pH measurements depends greatly on the selection of a suitable indicator, which in turns depends primarily on the anticipated pH of the sample. The commonly used indicator m-Cresol Purple (mCP) has an optimal range of 7.1 – 8.1. But for surface ocean, pH is often greater than 8.1 (ca. 8.6 in highly productive plume water), which is out of the optimal range of mCP. In this case, thymol blue (TB), with an optimal range of 7.6-8.6, is often used as the indicator for surface samples. For the oceanic pH range (7.3 – 8.5, as requested by the OOI), there is **no single indicator** that will cover this measurement range with optimal performance. The scientists acknowledge that the commercial off the shelf (COTS) pH sensors, including those considered to be ‘the best in the business’ and used worldwide, are only designed to carry one indicator (mCP, TB, or other indicator), and thus cannot achieve the optimal measurement performance for the entire oceanic pH range that may be encountered(2,3). Measurements made on the high or low end may be less precise, due to limitations of either chemical indicator. The precision and accuracy of pH measurements are most important in surface waters, where greater variability between measurements is likely to be found. However, surface waters generally have higher pH. The lowest pH waters are usually found in the stable deeper layers below 500-600 meters in open ocean, and these values are typically more stable temporally. The scientists also acknowledge that the current COTS sensor the OOI purchases may be the best available sensor, yet still not meet every threshold performance requirement in the pH sensor specification for fixed platforms and suffer from the single-indicator limitation.
Figure 1. Global distribution of pH values measured in situ. Seawater pH values below 7.5 are limited in number, however there will be instances that OOI sensors will encounter these conditions (e.g. in the North Pacific- Station PAPA and RSN) – source G. Proskurowski and RSN contractor.
Figure 2. North Pacific Ocean pH along 152_W in 2006 (pHT, 25_C). Reprinted from Byrne et al 2010.

Figure 2. Northeast Pacific Ocean pH by depth and latitude (from Byrne et al, 2010).
3.4 Revision History
No revisions to date.

4 Implementation

4.1 Overview
The conversion from L0 to the L1 pH of seawater data product is implemented using the Equation 2 in Section 3.2 and the code provided in Appendix A.

4.2 Inputs
Level 0 signal intensity data from the PHSEN instrument represent A (absorbance) at each wavelength needed for the L1 data equation (434 and 578 nm). L0 PH434SI is the intensity measurement of the wavelength 434nm and L0 PH578SI is the intensity measurement of the wavelength 578nm. Signal intensities can range from 0 to 4096 (unitless).

L0 ABSTHRM is the thermistor resistivity, which is needed to determine the salinity and temperature-dependent molar absorptivities required for the pH calculation.

Inputs are:

- L0 PH434SI signal intensity at 434nm ranging from 0 to 4096 (corresponds to a direct current volt range of 0 to 5).
- L0 PH578SI signal intensity at 578nm ranging from 0 to 4096 (corresponds to a direct current volt range of 0 to 5).
- L0 ABSTHRM thermistor resistivity with a DC volt range of 0 to 5.
- Wavelengths used to evaluate pH blank and sample absorptivities. These are set by the instrument firmware and are 434 nm and 578 nm for all OOI PHSEN instruments. These two wavelengths should be stored as metadata.
- ei - salinity and temperature-dependent ratios of the mCP molar absorptivities. These values are based upon test results of the reagent batches supplied by the vendor and are pre-loaded onto the instrument firmware. These differ between reagent batches and should be stored as metadata
- Preset constant 35 salinity unless using Additional input from attached CTD*.

*Additional optional input if PHSEN instrument is attached to a SeaBird CTD:
  - L2 PRACSAL practical salinity based on the most recent measurements from an attached CTD. See Appendix E for a list of the reference designators for all pH instruments for which this applies.

Input Data Format

Raw Record Structure
There are 2 main types of records recorded by the instrument: data records and information records. Information records note events such as 'start', 'stop', 'battery low' and possible errors.

Computed fields
The three L0 data values used to calculate the pH of seawater data product are contained in a floating decimal string as described below. Computed fields consist of data derived from the raw records. If the user wants to log data externally, the client software has the capability of reading text files with the logged hex strings described below. The only requirement is that each record is written to a separate line in the file.
Following the identifiers, all records begin with a byte containing length count. The length count includes the length and checksum bytes. A record can be up to 255 bytes long. The second byte is record type. The next 4 bytes are the time, seconds since Jan 1, 1904 GMT (total seconds).

**Example:**

This string is the beginning of a SAMI-pH record sent over the serial port:

*BFE70AC8EF9AF8...

The '*' indicates a record is to follow. The ‘BF’ represents a hash of the SAMI name and the stored validation values (a unique identifier). ‘E7’ is hexadecimal for 231 and is the length of the record. ‘0A’ (10 decimal) indicates this is a pH record. ‘C8EF9648’ is the date/time in seconds and translates to October 28, 2010 21:26 GMT.

All records end with a 1 byte checksum - the low byte of the sum of the bytes including the length and type. This is used for error checking of the transmission.

**SAMI-pH Data Records**

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<tr>
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<td>Type</td>
</tr>
<tr>
<td>4</td>
<td>Time</td>
</tr>
<tr>
<td>2</td>
<td>Starting thermistor</td>
</tr>
<tr>
<td>32</td>
<td>16 sets of reference light measurements (2 bytes ea.)</td>
</tr>
<tr>
<td>184</td>
<td>23 sets of 4 light measurements (2 bytes ea.)</td>
</tr>
<tr>
<td>2</td>
<td>(not used currently)</td>
</tr>
<tr>
<td>2</td>
<td>Battery</td>
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<tr>
<td>2</td>
<td>Thermistor</td>
</tr>
<tr>
<td>1</td>
<td>Checksum</td>
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On-board reference standard(s) (a.k.a. On-board Tris accuracy system) can be used to periodically update relative absorbance, as invoked by a marine operator or at pre-determined intervals recommended by the vendor (every 4-5 days is recommended), but frequency of this test would depend upon deployment length and sampling frequency. This test report does not rebaselne the instrument but appears as a separate metadata stream with a different data type (for the Sunburst SAMI-II it is data type 11 as opposed to data type 10 which is used for routine samples).

Range checks on the inputs are as part of the global range check (GLBLRNG, DCN 1341-10004) specified in the PHSEN Processing Flow documents (DCN 1342-00510). A separate range check on the inputs does not need to be applied.

The sample processing interval must be offset at no less than 4 minutes for the colorimetric reaction to occur (which takes 2.1 minutes after the period of pumping to gather the sample and perform the blank) and to account for pump timing (which can only be set in whole number minutes, not fractions).

### 4.3 Processing Flow

The specific steps necessary to create all calibrated and quality controlled data products for each OOI core instrument are described in the instrument-specific Processing Flow documents (DCN 1342-XXXXX). These processing flow documents contain flow diagrams detailing all of the
specific procedures (data product and QC) necessary to compute all levels of data products from the instrument and the order in which these procedures are to be applied.

The processing flow for the pH of seawater computation is as follows:

Step 1:
The instrument-specific information must be captured from the most-recent factory calibration sheet. The marine operator must perform the field/shipboard determination of blank and reference standard procedure using the on-board blanks and standards (a.k.a. On-board Tris accuracy system). The information from field/shipboard calibration is saved as instrument metadata to be provided to CI immediately post-deployment to 'update' the automated pre-deployment (L1b) data QC equations applied to the real-time data. The instrument can then be deployed.

Step 2:
The conversion of absorbance (L0 PH578SI and L0 PH434SI) and salinity/temperature (L0 ABSTHERM) from the instrument to pH of seawater data product (L1 PHWATER) is straightforward using the equation:

\[ \text{pH} = \text{pK}'a + \log \left( \frac{(R-e_1)/(e_2-Re_3)} \right) \]

The pKa’ is the indicator salinity and temperature-dependent equilibrium constant, R is the absorbance ratio A578/A434 corresponding to the peak absorbances of the unprotonated and protonated forms of the indicator (in this case mCP). The ei are the salinity and temperature-dependent ratios of the mCP molar absorptivities available from the vendor and preset in the firmware.

Step 3:
The appropriate automated QC tests are global range, spike, stuck value, local range, and temporal spatial gradient tests may be applied. However, the nature of local pH conditions make it difficult to set the parameters for all these tests with certainty at first deployment. Data should better inform these parameter limits on a location-specific and depth-specific basis.

4.4 Outputs
The output of the pH of seawater computation is
- L1a pH of seawater (unitless) as a decimal floating point number %.

The OOI Level 2 science program requirement for accuracy is +/-0.01, precision is +/- 0.005, and drift of not more than 0.01 of pH of seawater.

The metadata that must be included with the output are
- Time
- Temperature in degrees C
- Salinity (either as default of 35 or as reported by the attached SeaBird CTD)
- Reference standard and blank absorbances used in this calculation during field/shipboard calibration
- Any corresponding post-deployment or at-recovery field pH in situ measurements, or post-recovery drift corrections determined at the time of annual factory service used to refine the above field calibration factor for L1b or L1c data.
4.5 Computational and Numerical Considerations

4.5.1 Numerical Programming Considerations
There are no numerical programming considerations for this computation. No special numerical methods are used.

4.5.2 Computational Requirements
There are no computational limitations or requirements.

4.6 Code Verification and Test Data Set
The code will be verified using the test data set provided, which contains inputs and their associated correct outputs. CI will verify that the code is correct by checking that the output, generated using the test data inputs, is identical to the test data output.

Test Data Input:
*A3E70ACAB31FB05B007DD066A074708A607E00669074B08A207E20669074B08A207E206
67074D0
8A307E5066B074D08A407E2066B074C08A307E2065F074908D07DB05EB0745076307E304
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Data Product Specification for pH of Seawater

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<td>25.8029</td>
<td>8.0520</td>
</tr>
<tr>
<td>10.0000</td>
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<td>11.4917</td>
<td>25.7845</td>
<td>8.0628</td>
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<td>11.4880</td>
<td>25.7937</td>
<td>8.0565</td>
</tr>
</tbody>
</table>
Appendix A  Example Code
Matlab Code example below was provided by the vendor Sunburst Sensors LLC. It captures all of the DPS steps above and reflects the software the Sunburst-SAMI instrument currently uses. One external reviewer questioned the use of the steps noted below and the vendor’s recommendation is included for posterity.

Notes specific to section of this example matlab code:
% Average Temperature: The SAMI takes a temperature measurement at the beginning of the sample (prior to flushing) and there's another temperature measurement at the end of the measurement cycle. The entire sample takes ~3 minutes but the actual pH measurement is done during the last 46 seconds. Sunburst's recommendation for OOI coders is to just use the 2nd temperature measurement for the calculation of R instead of the average temperature step captured here in this code.

% pKa from Clayton/Byrne 1993: This is the pKₐ calculation that will change slightly in the late 2012 software upgrade. Updated example matlab code to reflect the changes will be included in a revised PHWATER DPS when this occurs. Sunburst is using dye purification methods described in Lui et al (2011), however, the equations may differ slightly because the molar absorptivities must be known for this instrument in order to calculate the indicator concentration that is needed to extrapolate to zero indicator.

% Determine the most linear region of points for seawater calculation
% Skip first 5 points: This code selects the most linear region of measurement points dynamically instead of using a set of static points from the SAMI instrument. This is necessary because if there is significant biofouling or a partial block at the sample inlet port, the points in the curve will shift due to the lower flow rate. The example code provided uses the best 7 points by using a moving filter to find the best R^2. Sunburst strongly recommends OOI implements an identical step in the code.

% ************************************************************
% SAMI2-pH Telemetry Program
% This m-file will read in raw data hex strings that are output from the
% SAMI2-pH instrument and process and output:
% - Time
% - pH
% - Temperature
% ****************************
% clear all
% Constants
cp = 1; % cell path length
% Molar absorptivities - unique to indicator lot
ea434=17709;
ea578=107;
eb434=2287;
eb578=38913;
eaTemp=24.8000;
ebTemp=24.8600;
Inta434 = ea434 + 24.5250*eaTemp;
Inta578 = ea578 - 0.5869*eaTemp;
Intb434 = eb434 - 6.2231*ebTemp;
Intb578 = eb578 + 99.6170*ebTemp;
Salinity=35;
% ************************************************************************
% Select the SAMI-pH file to analyze
[File, myPath] = uigetfile('*.*', 'Select the file to analyze');
cd(myPath);
fid = fopen(File);

% Path name for saving output files
fname = [myPath, File];
outfile = strcat(fname(1:end-4), '_out1.txt'); % path for saving data files

% ******************* Read in hex data from SAMI2-pH *******************
% Search for start string of data '*'----0A' where - is any hex char.
% Fgetl returns -1 on EOF to end loop.
i = 1; j = 1;
while 1
    s = fgetl(fid);
    if s == -1, break, end % indicates EOF
        if (strcmpi('*', s(1:1)) == 1 && strcmpi('0A', s(6:7)))
            s = s(2:length(s)); % Truncate to beginning of measurement
            while length(s) < 464
                s = [s, fgetl(fid)];
            end
            AA(i,:) = s;
            i = i + 1;
        else
        end
    end
end
fclose(fid);

[s1, s2] = size(AA);

% Extract data from hex string
for i = 1:s1
    Type(i) = hex2dec(AA(i, 5:6)); % Type 10 - measurement
% Date/Time
    Time(i) = hex2dec(AA(i, 7:14));
    dt(i) = (Time(i) / (60 * 60 * 24));
    [y(i), m(i), d(i), h(i), mn(i), s(i)] = datevec(dt(i));
    y2(i) = y(i) + 1904;
    Date(i,:) = datestr(datenum([y2(i), m(i), d(i), h(i), mn(i), s(i)]), 'mmmm dd, yyyy HH:MM:SS');
    datetime1(i) = (Time(i) / (60 * 60 * 24));

    Temp1(i) = hex2dec(AA(i, 15:18)); % Temp taken at beginning of measurement
    chksum = hex2dec(AA(i, 463:464)); % Checksum
    Temp2(i) = hex2dec(AA(i, 459:462)); % Temp taken at end of measurement
    Batt(i) = hex2dec(AA(i, 455:458)); % Battery voltage

% Raw blank measurements (4 total)
    Ref434A(i,:) = hex2dec(AA(i, 19:22));
    Sig434A(i,:) = hex2dec(AA(i, 23:26));
    Ref578A(i,:) = hex2dec(AA(i, 27:30));
    Sig578A(i,:) = hex2dec(AA(i, 31:34));

    Ref434B(i,:) = hex2dec(AA(i, 35:38));
    Sig434B(i,:) = hex2dec(AA(i, 39:42));
    Ref578B(i,:) = hex2dec(AA(i, 43:46));
    Sig578B(i,:) = hex2dec(AA(i, 47:50));

    Ref434C(i,:) = hex2dec(AA(i, 51:54));
Data Product Specification for pH of Seawater

\[
\text{Sig434C}(i,:) = \text{hex2dec}(\text{AA}(i,55:58));
\]
\[
\text{Ref578C}(i,:) = \text{hex2dec}(\text{AA}(i,59:62));
\]
\[
\text{Sig578C}(i,:) = \text{hex2dec}(\text{AA}(i,63:66));
\]
\[
\text{Ref434D}(i,:) = \text{hex2dec}(\text{AA}(i,67:70));
\]
\[
\text{Sig434D}(i,:) = \text{hex2dec}(\text{AA}(i,71:74));
\]
\[
\text{Ref578D}(i,:) = \text{hex2dec}(\text{AA}(i,75:78));
\]
\[
\text{Sig578D}(i,:) = \text{hex2dec}(\text{AA}(i,79:82));
\]

% Blank absorbances
\[
\text{Blank434A}(i,:) = \text{Sig434A}(i,:) / \text{Ref434A}(i,:);
\]
\[
\text{Blank578A}(i,:) = \text{Sig578A}(i,:) / \text{Ref578A}(i,:);
\]
\[
\text{Blank434B}(i,:) = \text{Sig434B}(i,:) / \text{Ref434B}(i,:);
\]
\[
\text{Blank578B}(i,:) = \text{Sig578B}(i,:) / \text{Ref578B}(i,:);
\]
\[
\text{Blank434C}(i,:) = \text{Sig434C}(i,:) / \text{Ref434C}(i,:);
\]
\[
\text{Blank578C}(i,:) = \text{Sig578C}(i,:) / \text{Ref578C}(i,:);
\]
\[
\text{Blank434D}(i,:) = \text{Sig434D}(i,:) / \text{Ref434D}(i,:);
\]
\[
\text{Blank578D}(i,:) = \text{Sig578D}(i,:) / \text{Ref578D}(i,:);
\]
% Average blank absorbance
\[
\text{blank434}(i,:) = (\text{Blank434A}(i,:) + \text{Blank434B}(i,:) + \text{Blank434C}(i,:) + \text{Blank434D}(i,:)) / 4;
\]
\[
\text{blank578}(i,:) = (\text{Blank578A}(i,:) + \text{Blank578B}(i,:) + \text{Blank578C}(i,:) + \text{Blank578D}(i,:)) / 4;
\]
% Reference and signal measurement raw intensities
\[
j = 1;
\]
\[
\text{for} \ ii = 83:16:30
\]
\[
\text{Ref434}(i,j) = \text{hex2dec}(\text{AA}(i,ii:ii+3));
\]
\[
\text{l434}(i,j) = \text{hex2dec}(\text{AA}(i,ii+4:ii+7));
\]
\[
\text{Ref578}(i,j) = \text{hex2dec}(\text{AA}(i,ii+8:ii+11));
\]
\[
\text{l578}(i,j) = \text{hex2dec}(\text{AA}(i,ii+12:ii+15));
\]
\[
j = j + 1;
\]
\[
\text{end}
\]
% Thermistor calculations
\[
\text{Rt1}(i) = (\text{Temp1}(i)/(4096-\text{Temp1}(i))) \times 17400;
\]
\[
\text{InvT1}(i) = 0.0010183 + 0.000241 \times (\log(\text{Rt1}(i))) + 0.00000015 \times (\log(\text{Rt1}(i)))^3;
\]
\[
\text{TempK1}(i) = 1 / \text{InvT1}(i);
\]
\[
\text{TempC1}(i) = \text{TempK1}(i) - 273.15;
\]
\[
\text{TempF1}(i) = 1.8 \times \text{TempC1}(i) + 32;
\]
\[
\text{TempFinal1}(i) = \text{TempC1}(i);
\]
\[
\text{Rt2}(i) = (\text{Temp2}(i)/(4096-\text{Temp2}(i))) \times 17400;
\]
\[
\text{InvT2}(i) = 0.0010183 + 0.000241 \times (\log(\text{Rt2}(i))) + 0.00000015 \times (\log(\text{Rt2}(i)))^3;
\]
\[
\text{TempK2}(i) = 1 / \text{InvT2}(i);
\]
\[
\text{TempC2}(i) = \text{TempK2}(i) - 273.15;
\]
\[
\text{TempF2}(i) = 1.8 \times \text{TempC2}(i) + 32;
\]
\[
\text{T}(i) = (\text{TempC1}(i) + \text{TempC2}(i)) / 2;
\]
% Average Temperature
\[
\text{TempFinal}(i) = \text{mean}(T);
\]
\[
\text{end}
\]
\[
\text{Ref434} = \text{Ref434}'; \ i434 = i434'; \ i578 = i578'; \text{Ref578} = \text{Ref578}';
\]
\[
[d3,d4] = \text{size}(i434);
\]
\[
\text{for} \ j = 1:d4
\]
% Absorbances
\[
\text{A434}(i,:) = -\log10(\text{l434}(i,:)/\text{Ref434}(i,:));
\]
\[
\text{A578}(i,:) = -\log10(\text{l578}(i,:)/\text{Ref578}(i,:));
\]
\[
\text{end}
\]
A434blank(1:d3,j)=log10(blank434(j));
A578blank(1:d3,j)=log10(blank578(j));

Abs434(:,j)=A434(:,j)-A434blank(:,j);
Abs578(:,j)=A578(:,j)-A578blank(:,j);

% pKa from Clayton/Byrne 1993
pKa(:,j)=((1245.69./(TempFinal(j)+273.15))+3.8275+(0.0021*(35-Salinity)));
R(:,j) = (A578(:,j)-A578blank(:,j))./(A434(:,j)-A434blank(:,j));

% Molar absorptivities
Ea434(:,j) = -24.525*TempFinal(j) + Inta434;
Ea578(:,j) = 0.5869*TempFinal(j) + Inta578;
Eb434(:,j) = 6.2231*TempFinal(j) + Intb434;
Eb578(:,j) = -99.617*TempFinal(j) + Intb578;

e1(:,j) = Ea578(:,j)./Ea434(:,j);
e2(:,j) = Eb578(:,j)./Ea434(:,j);
e3(:,j) = Eb434(:,j)./Ea434(:,j);

V1(:,j)=R(:,j)-e1(:,j);
V2(:,j)=e2(:,j)-R(:,j).*e3(:,j);

% Indicator concentration calculations
HI(:,j)=(Abs434(:,j).*Eb578(:,j))-(Abs578(:,j).*Eb434(:,j))./((Ea434(:,j).*Eb578(:,j))-(Eb434(:,j).*Ea578(:,j)));
I(:,j)=(Abs578(:,j).*Ea434(:,j))-(Abs434(:,j).*Ea578(:,j))./((Ea434(:,j).*Eb578(:,j))-(Eb434(:,j).*Ea578(:,j)));

% Use data points that are in linear region
IndConc(:,j)=HI(:,j)+I(:,j);
pointpH(:,j)=real(pKa(:,j)+log10(V1(:,j)./V2(:,j)));

% Determine the most linear region of points for seawater calculation
% Skip first 5 points
IndConca(:,j)=IndConc(6:d3,j);
Y(:,j)=pointpH(6:d3,j);
X=[1:1:d3-5];

step=7; % # of pts to use
for ii=1:length(X)-step
    sumxa(ii,j)=sum(X(ii:ii+step));
    sumya(ii,j)=sum(Y(ii:ii+step,j));
    sumxya(ii,j)=sum(X(ii:ii+step).*Y(ii:ii+step,j));
    sumx2a(ii,j)=sum(X(ii:ii+step).^2);
    sumy2a(ii,j)=sum(Y(ii:ii+step,j).^2);
    avgxa(ii,j)=mean(X(ii:ii+step));
    avgya(ii,j)=mean(Y(ii:ii+step,j));
    sumxx2a(ii,j)=sumxa(ii,j).*sumxa(ii,j);
    sumyy2a(ii,j)=sumya(ii,j).*sumya(ii,j);
    ssxya(ii,j)=sumxya(ii,j)-(sumxa(ii,j).*sumya(ii,j));
    ssx2a(ii,j)=sumx2a(ii,j)-(sumxx2a(ii,j)/count);
    ssy2a(ii,j)=sumy2a(ii,j)-(sumyy2a(ii,j)/count);
slopea(ii,j)=ssxya(ii,j)./ssxa(ii,j);
r2a(ii,j)=((ssxya(ii,j).^2)./(ssxa(ii,j).*ssya(ii,j)));
end

% Range of seawater points to use
[xia,yia]=max(r2a(:,j)); % Find start point of the best fit using best R-squared
cutoff1(j)=yia;           % Start point

cutoff2(j)=yia+step;      % End point

IndConcS(:,j)=IndConca(cutoff1(j):cutoff2(j),j);
pointpHS(:,j)=real(Y(cutoff1(j):cutoff2(j),j));
[a1(j) a2(j)]=size(pointpHS);

% ********************************************

% *************** Final pH Calcs **********************

sumx(1,j)=sum(IndConcS(:,j));
sumy(1,j)=sum(pointpHS(:,j));
sumxy(1,j)=sum((pointpHS(:,j).*IndConcS(:,j)));
sumx2(1,j)=sum((IndConcS(:,j).^2));
sumy2(1,j)=sum((pointpHS(:,j).^2));

xbar(1,j)=mean(IndConcS(:,j));
ybar(1,j)=mean(pointpHS(:,j));

sumxx2(:,j)=sumx(1,j).*sumx(1,j);
sumyy2(:,j)=sumy(1,j).*sumy(1,j);
ssxy(1,j)=sumxy(1,j) - (sumx(:,j)*sumy(:,j))/a1(j);
ssx(1,j)=sumx2(1,j) - (sumxx2(:,j)/a1(j));
ssy(1,j)=sumy2(1,j) - (sumyy2(:,j)/a1(j));
slope(1,j)=ssxy(1,j)/ssx(1,j);
FinalpH(1,j)=ybar(1,j)-slope(1,j).*xbar(1,j);
end

% ************************ Figures **********************

X2=[1:1:d3];

figure
plot(X2,Ref434,'bo',X2,Ref578,'ro')
title('Reference Signals');ylabel('Reference')
grid on, axis tight

figure
plot(X2,I434,'.b',X2,I578,'.r')
title('Intensity Signals');ylabel('Signals')
grid on, axis tight

X2=X2';

% Plot of seawater point pH
figure
plot(real(pointpH),'.-')
title('Sea Point pH');ylabel('pH')
grid on, axis tight

x1=[1:1:length(FinalpH)];

% Plot of Seawater Final pH
figure
[AX,H1,H2]=plotyy(x1,FinalpH,x1,TempFinal);
set(get(AX(1),'Ylabel','String','Final Sea pH'))
set(get(AX(2),'Ylabel','String','Temp (C)'))
set(H1,'LineStyle','-','marker','.')
set(H2,'LineStyle','-','marker','.')
grid on

% *************************************************************************
% Output file
fid = fopen(outfile,'w');
fprintf(fid,'%8.4f %8.4f %8.4f
');
fmt = '%8.4f %8.4f %8.4f
';
data=[Time; TempFinal; FinalpH];
fprintf(fid,fmt,data);
fclose(fid);
Appendix B  Output Accuracy
The DOORS accuracy requirement for pH is +/-0.01 units and the objective is to have accuracy of +/-0.005 units. The statement of accuracy by the manufacturer is +/-0.003 units.

Appendix C  Sensor Calibration Effects
This instrument must be calibrated at expected in situ temperatures and to the appropriate standard (mCP or TB) for reading expected in the area of deployment. There is a shelf life and holding requirements for the reagents/standards/onboard blank available from the manufacturer. Care should be taken to calibrate the instrument just prior to deployment using the appropriate standard and reagents that are confirmed to not be expired (and will not run past the expiration date during deployment) and were held in cool dark environments prior to use.

It is recommended that deployments start with a blank cycle, but for some testing a user may wish not to do this.

The ‘Warm-Up Interval’ allows the external device to stabilize before measuring and should be set in accordance with manufacturers suggestions.

The ‘# samples to average’ allows multiple readings to be averaged. The power selection allows devices that have their own power conditioning to access the instrument batteries directly and thereby increase efficiency. The instrument will need to be flushed after each deployment in seawater (see manual for flushing procedure description).

During pre-deployment evaluations: If any signal intensity is at or near 4000, the channel may be saturated with light, giving erroneous results. Reference and blank signal intensities should be greater than ~1500. Lower intensities will result in higher noise in absorbance and thus pH measurements. However, if during blank measurement signal intensities are low but reference intensities are not, the flow cell needs to be flushed. Dark signals will normally range from ~50 – 200. Higher or erratic dark signals could indicate an electronic problem with the instrument. Onshore the instrument comes with a DI reagent bag to perform flushing. Again, a marine operator can send a command to do this following visual QC inspection of the data or a flushing subroutine can be run periodically at pre-determined intervals, but this would be flushed with seawater in situ instead of DI water. Dark signals will normally range from ~50 – 200. Higher or erratic dark signals could indicate an electronic problem with the instrument. All these ‘checks’ would be part of the Human-in-the-loop QAQC procedures at the marine IOs during predeployment field verification testing or after ‘bad’ quality data flags appear in the data stream.

Appendix D  Sample Factory Characterization Sheet
To be provided at time of DPS signature
Appendix E  Collocated CTD Lookup Table for PHWATER Data

Consult the following table to determine the appropriate CTD instrument from which to draw data in order to compute the corrected PHWATER data product. Each pair of collocated instruments is highlighted in blue. Cells highlighted in yellow indicate pairs not co-located as of August 2012, but may be modified through future ECR to make the pairs co-located. (Note that the last four digits of the References Designator may change once the new instrument series and sequence numbers are updated, October 2012).

<table>
<thead>
<tr>
<th>Reference Designator</th>
<th>Subsite Name</th>
<th>Site Suffix</th>
<th>Node Type</th>
<th>Instrument Class</th>
<th>Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA03FLMA-RI001-07-CTDMO0999</td>
<td>Argentine Basin Mesoscale Flanking Mooring A</td>
<td>FLMA</td>
<td>RI (Mooring Riser)</td>
<td>CTDMO</td>
<td>40</td>
</tr>
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<td>GA03FLMA-RI001-02-PHSEN0999</td>
<td>Argentine Basin Mesoscale Flanking Mooring A</td>
<td>FLMA</td>
<td>RI (Mooring Riser)</td>
<td>PHSEN</td>
<td>40</td>
</tr>
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<td>GA03FLMB-RI001-07-CTDMO0999</td>
<td>Argentine Basin Mesoscale Flanking Mooring B</td>
<td>FLMB</td>
<td>RI (Mooring Riser)</td>
<td>CTDMO</td>
<td>40</td>
</tr>
<tr>
<td>GA03FLMB-RI001-02-PHSEN0999</td>
<td>Argentine Basin Mesoscale Flanking Mooring B</td>
<td>FLMB</td>
<td>RI (Mooring Riser)</td>
<td>PHSEN</td>
<td>40</td>
</tr>
<tr>
<td>GA01SUMO-RI003-03-CTDMO0999</td>
<td>Argentine Basin Surface Mooring</td>
<td>SUMO</td>
<td>RI (Mooring Riser)</td>
<td>CTDMO</td>
<td>20</td>
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<td>GA01SUMO-RI003-01-PHSEN0999</td>
<td>Argentine Basin Surface Mooring</td>
<td>SUMO</td>
<td>RI (Mooring Riser)</td>
<td>PHSEN</td>
<td>20</td>
</tr>
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<td>GA01SUMO-RI003-06-CTDMO0999</td>
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<td>SUMO</td>
<td>RI (Mooring Riser)</td>
<td>CTDMO</td>
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<tr>
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<td>SUMO</td>
<td>RI (Mooring Riser)</td>
<td>PHSEN</td>
<td>100</td>
</tr>
<tr>
<td>RS03AXVM-PC03A-08-CTDPFA303</td>
<td>Axial Mooring</td>
<td>AXVM</td>
<td>PC (Platform Interface Controller)</td>
<td>CTDPF</td>
<td></td>
</tr>
<tr>
<td>RS03AXVM-PC03A-10-PHSENA302</td>
<td>Axial Mooring</td>
<td>AXVM</td>
<td>PC (Platform Interface Controller)</td>
<td>PHSEN</td>
<td></td>
</tr>
<tr>
<td>RS03AXVM-SF03A-09-CTDPFA302</td>
<td>Axial Mooring</td>
<td>AXVM</td>
<td>SF (Shallow Profiler Science Float)</td>
<td>CTDPF</td>
<td></td>
</tr>
<tr>
<td>RS03AXVM-SF03A-12-PHSENA301</td>
<td>Axial Mooring</td>
<td>AXVM</td>
<td>SF (Shallow Profiler Science Float)</td>
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<tr>
<td>CE01ISSM-MF005-01-CTDBP0999</td>
<td>Endurance OR Inshore Surface Mooring</td>
<td>ISSM</td>
<td>MF (Multi-Function Node)</td>
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<td>23</td>
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<td>ISSM</td>
<td>MF (Multi-Function Node)</td>
<td>PHSEN</td>
<td>23</td>
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<td>RI (Mooring Riser)</td>
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<td>CE01ISSM-RI002-03-PHSEN0999</td>
<td>Endurance OR Inshore Surface Mooring</td>
<td>ISSM</td>
<td>RI (Mooring Riser)</td>
<td>PHSEN</td>
<td>5</td>
</tr>
<tr>
<td>CE04OSSM-PC01B-03-PHSENA106</td>
<td>Endurance OR Offshore Hybrid Profiler Mooring</td>
<td>OSHY</td>
<td>PC (Platform Interface Controller)</td>
<td>PHSEN</td>
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</tr>
<tr>
<td>CE04OSSM-RI002-05-CTDBP0999</td>
<td>Endurance OR Offshore Surface Mooring</td>
<td>OSSM</td>
<td>RI (Mooring Riser)</td>
<td>CTDBP</td>
<td>5</td>
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<tr>
<td>CE04OSSM-RI002-03-PHSEN0999</td>
<td>Endurance OR Offshore Surface Mooring</td>
<td>OSSM</td>
<td>RI (Mooring Riser)</td>
<td>PHSEN</td>
<td>5</td>
</tr>
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<td>Code</td>
<td>Description</td>
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<td>------------</td>
<td>--------------</td>
<td>-----------</td>
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<tr>
<td>CE02SHBP-LJ01D-02-CTDBPD102</td>
<td>Endurance OR Shelf Benthic Pkg</td>
<td>SHBP</td>
<td>BJ (LP Jbox)</td>
<td>CTDBP</td>
<td></td>
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