DATA PRODUCT SPECIFICATION
FOR PARTIAL PRESSURE OF CO₂ IN SEAWATER

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Signature Page

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

OOI Chief Systems Engineer: ________________________________

Date: 2012-06-18

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

OOI CI Signing Authority: ________________________________

Date: 2012-06-18
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1 Abstract

This document describes the procedure used to obtain the OOI Level 1 Partial Pressure of CO₂ (pCO₂) in Seawater data product, which is calculated using the output from the Sunburst SAMI²-CO₂. Partial pressure of a gas dissolved in water is understood as the partial pressure in air that the gas would exert in a hypothetical air volume in equilibrium with that water. This document is intended to be used by OOI programmers to construct appropriate processes to create the L1 data product.

2 Introduction

2.1 Author Contact Information

Please contact Michael Vardaro (mvardaro@coas.oregonstate.edu) or the Data Product Specification lead (DPS@lists.oceanobservatories.org) for more information concerning the computation and other items in this document.

2.2 Metadata Information

2.2.1 Data Product Name

The OOI Core Data Product Name for this product is
- PCO2WAT

The OOI Core Data Product Descriptive Name for this product is
- Partial pressure of CO₂ in seawater

2.2.2 Data Product Abstract (for Metadata)

The pCO₂ data product PCO2WAT is the partial pressure of CO₂ in seawater, which is the pressure that would be exerted by CO₂ if all other gases were removed. Partial pressure of a gas dissolved in water is understood as the partial pressure in air that the gas would exert in a hypothetical air volume in equilibrium with that water. pCO₂ in the ocean is determined by measuring the amounts of dissolved CO₂ and HCO₃⁻, in this case by using an optical cell to measure the colorimetric equilibration of a pH sensitive chemical reagent.

2.2.3 Computation Name

Not required for data products.

2.2.4 Computation Abstract (for Metadata)

The OOI Level 1 Partial Pressure of CO₂ in Seawater core data product is computed internally using calibration constants and the temperature-corrected CO₂ measurement made using onboard measurements of temperature and optical absorbance.

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
- pCO₂

2.2.7 Similar Data Products

Similar products that this data product may be confused with are PCO2ATM and PCO2SSW, the data product for the partial pressure of CO₂ in atmosphere and surface seawater respectively.
2.3 Instruments
For information on the instruments from which the L1 Partial pressure of CO₂ in seawater core data product inputs are obtained, see the PCO2W flow document (1342-00490). This document contains information on the instrument class and make/model; it also describes the flow of data from the SAMI²-CO₂ 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.

2.4 Literature and Reference Documents
Sunburst Operating Manual AFT/SAMI²-CO₂
(see DPS Artifacts >> CO2 MANUAL SAMI AFT combined.pdf)
SAMII Record Format Documentation
(see DPS Artifacts >> SAMI_Record_Format.pdf)
(see DPS Artifacts >> Grandpre & Baehr_1999 (pCO2 sensors).pdf)

2.5 Terminology

2.5.1 Definitions
Definitions of general OOI terminology are contained in the Level 2 Reference Module in the OOI requirements database (DOORS).

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.

SAMI = Submersible Autonomous Moored Instrument, specifically the Sunburst SAMI²-CO₂

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

CalT, CalA, CalB, and CalC = Calibration coefficients provided by the manufacturer (unique to each instrument and each calibration) in written and digital form after every calibration or refurbishment cycle.

Ea434, Ea620, Eb434, and Eb620 = equilibration constants for the indicator solution at 434 nm and 620 nm wavelengths of light, provided by the manufacturer in written and digital form after every calibration or refurbishment cycle.

Tcor_RCO₂ = the temperature-corrected CO₂ measurement made using onboard measurements of temperature and optical absorbance
RCO₂₁ = the SAMI response, calculated using the equilibration solution pH at infinite dilution, which can be described using a combination of the indicator equilibrium expression with Beer’s law (DeGrandpre, et al. 1999).
Tcoeff = Temperature coefficient derived from the SAMI response (RCO₂₁) at calibration temperatures
TempC = Temperature in °C, derived from the thermistor raw value (Therm)
3 Theory

3.1 Description

The partial pressure of carbon dioxide (pCO$_2$) is determined by equilibrating a pH sensitive indicator solution (Bromothymol Blue) to the sampled seawater. Aqueous carbon dioxide in seawater diffuses across the permeable silicon membrane equilibrator producing a color change in the indicator solution. The equilibrated indicator solution is pumped through an optical cell where the optical absorbance is measured at the two wavelengths corresponding to the peak absorbances for the protonated and deprotonated forms of the indicator. By calibrating the instrument’s response over the range of interest and compensating for temperature using an onboard thermistor, the pCO$_2$ can be calculated based on the calibration curve. Periodic blanks are run every 3.5 days (an empirically derived interval) to correct for drift of the electro-optical system, while reference measurements of the LEDs correct for interim deviations (SAMI$^2$-CO$_2$ Manual).

3.2 Mathematical Theory

The equation used to calculate pCO$_2$ from the Sunburst SAMI instrument is:

\[
pCO_2 = 10^{((-1*CalB) + ((CalB^2) - (4*CalA*(CalC - Tcor_RCO_2)))^0.5) / (2*CalA))}
\]

The calibration coefficients (CalT, CalA, CalB, and CalC), unique to each instrument and each calibration, are provided by the manufacturer, along with the equilibration constants for the indicator solution at 434 nm and 620nm wavelengths (Ea434, Ea620, Eb434, and Eb620).

“Tcor_RCO$_2$” is the temperature-corrected CO$_2$ measurement made using onboard measurements of temperature and optical absorbance:

\[
Tcor_RCO_2 = RCO_2 + Tcoeff*(TempC - CalT)
\]

For a full description of the mathematical theory and equations behind the pCO2 measurement, see page 1154 of DeGrandpre, et al., 1999.

3.3 Known Theoretical Limitations

Instrument results are only valid between 0 – 35 °C

3.4 Revision History

No revisions to date.
4 Implementation

4.1 Overview

The included Matlab code (provided by J. Newton at Sunburst Sensors, LLC; see Appendix A) executes a step-by-step computation that converts the data from hexadecimal output into the desired science units, performs the necessary blank calibration, and temperature compensation (using onboard temperature measurements).

4.2 Inputs

Inputs are:

- Type 4 Raw SAMI\textsuperscript{2}-CO\textsubscript{2} serial output (hexadecimal format, 80 characters, see below for parsing of L0 inputs)
- Type 5 Blank measurement record serial output (hexadecimal format, see below for parsing)
- CalT, CalA, CalB, and CalC = Calibration coefficients unique to each instrument and each calibration, provided by the manufacturer in written and digital form after every calibration or refurbishment cycle. Stored as metadata.
- Ea434, Ea620, Eb434, and Eb620 = equilibration constants for the indicator solution at 434 nm and 620nm wavelengths of light, provided by the manufacturer in written and digital form after every calibration or refurbishment cycle. Stored as metadata.

Input Data Formats (as per the SAMI Record Format Documentation, pp. 1-2):

Records are stored and sent over the serial port in hexadecimal format. When sent over the serial link a record is preceded by "*" and a one byte hash of the SAMI name and calibration (a unique identifier). The client software uses these to recognize the start of a record, and discards them. Following that is the actual record, which begins with a length byte; this is a count including the length and checksum bytes, and can be up to 255 bytes long. The second byte is the record type. The next 4 bytes are the time, seconds since Jan 1 1904 GMT (totalSeconds).

The SAMI\textsuperscript{2}-CO\textsubscript{2} instrument has two types of records, the regular measurement (type 4) and the blank measurement records (type 5), which contain the following variables:

```matlab
Type(i)=hex2dec(AA(i,5:6));     % Type 4 - Measurement, Type 5 - Blank
Time(i)=hex2dec(AA(i,7:14));    % Time
DRef1(i)=hex2dec(AA(i,15:18));  % Dark Reference LED
DSig1(i)=hex2dec(AA(i,19:22));  % Dark Signal LED
R434(i)=hex2dec(AA(i,23:26));   % 434nm Reference LED intensity
S434(i)=hex2dec(AA(i,27:30));   % 434nm Signal LED intensity
R620(i)=hex2dec(AA(i,31:34));   % 620nm Reference LED intensity
S620(i)=hex2dec(AA(i,35:38));   % 620nm Signal LED intensity
Ratio434(i)=hex2dec(AA(i,39:42)); % 434nm Ratio
Ratio620(i)=hex2dec(AA(i,43:46)); % 620nm Ratio
Batt(i)=hex2dec(AA(i,71:74));   % Battery voltage
Therm(i)=hex2dec(AA(i,75:78));  % Thermistor raw value
```

Example of a type 4 SAMI\textsuperscript{2}-CO\textsubscript{2} record:

\`*5B2704C8EF9FC90FE06400FE8063C0FE3067460B1F0FE6065A0FE9067F0FE306A60CDE0FF3B\`
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 document (DCN 1342-00490). This processing flow document contains 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 should be carried out.

Step 1: Calibration constants are provided by the manufacturer and entered into the processing program.

Step 2: Download the hexadecimal type 4 raw measurement record (which contains the L0 data variables) and type 5 blank measurement records from the instrument.

Step 3: Implement the Matlab code provided in Appendix A to extract the required signal and temperature data for both the sample and blank analyses, correct the sample signal using the blank measurement, and calculate the temperature-corrected pCO$_2$ (in µatm).

Step 4: The final product is the temperature-corrected L1 pCO$_2$ in µatm units, along with the time stamp and temperature measurement from the SAMI instrument.

Step 5: Convert the time stamp from Serial Format into real date and time values. A serial date number represents the whole and fractional number of days from 1-Jan-0000 to a specific date. The year 0000 is merely a reference point and is not intended to be interpreted as a real year in time. See Working with Date Strings in the MATLAB Programming documentation for more information on creating or converting to a date string.

Step 6: Publish empty or dummy value upon computational error. See Processing Flow document (DCN 1342-00490) for additional post-processing steps.

4.4 Outputs

The outputs of the Measured pCO$_2$ computation are

- L1a PCO2WAT (pCO$_2$) in µatm, as a 7 character floating point number, %.4f

The metadata that must be included with the output are

- Date & Time as mm/dd/yy hh:mm:ss
- Temperature in °C, as a 6 character floating point number, %.4f
- The calibration coefficients used in the calculation (CalT, CalA, CalB, CalC, Ea434, Eb434, and Eb620)
- Depth, in meters (for mobile platforms only)

See Appendix B for a discussion of the accuracy of the output.

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

N/A
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 pCO2 output.

**Test Data Input:**

*7E1281CBACEE4900430000020000000002129A
*7E2705CBACEE7F007D007D0B2A00BF080500E00187034A008200790B2D00BE080600DE0C1406C98C
*7E2704CBACEE4CB008000880B2900B2080600D300FB0263007F00890B2B00B4080700CE0C5106C884
*7E2704CBACEF43007E00890B27014408070189045B0875007E00870B2B1040080201860C5506C601
*7E2704CBACEFBB007E00820B2A042B0803051F1618278500800850B2A043C08040590C5506C5A9
*7E2704CBACF033007F00840B28054D080606831CC330A007F00850B290551080406800C5606C556
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*7E2704CBACF19B008000750B2B01D20807023008310E94007E00730B2A01D2080502290C5706C0A2
*7E2704CBACF213008000740B2A01D50808042F08501FC6007D00780B3201D8080A04350C5706C0A5
*7E2704CBACF28B007F00710B2F0174080203570615189B008100730B2A0174080A03580C5706C125
*7E2704CBACF303007E006B0B2C019B080803CC07001CBA007F006F0B300199080803D00C5706C4E3
Test Data Output:

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<th>Data Type</th>
<th>Temperature (°C)</th>
<th>pCO2</th>
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<td>18.8526</td>
<td>0</td>
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<td>4</td>
<td>18.9725</td>
<td>280.0354</td>
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Appendix A  Example Code

% ************************************************************************
% SAMI2-CO2 Telemetry Program
% Provided by J. Newton at Sunburst Sensors, LLC
% This m-file will read in raw data hex strings that are output from the
% SAMI2-CO2 instrument and process and output:
% - Time
% - pCO2 in uatm
% - Temperature
% ************************************************************************
clear all
warning off all
% *************************** Constants ***********************************
% Calibration coefficients (unique to each instrument and each
% calibration)
CalT=16.5;
CalA=0.0459;
CalB=0.6257;
CalC=1.5406;
% *************** Select the SAMI output file to analyze *****************
[File,myPath]=uigetfile('*.*','Select the file to analyze');
cd(myPath);
fid = fopen(File);
% Path for saving data files
fname=[myPath,File];
outfile=strcat(fname(1:end-4),'_out.xls');

% ************************************************************************
% Extract data from hex string
% Read in SAMI hex data
i=1; j=1; k=1;
while 1
  s=fgetl(fid);
  if s == -1, break,end % indicates EOF
    if strcmpi('**',s(1:1))&& strcmpi('04',s(6:7))| strcmpi('05',s(6:7))
      s = s(2:length(s));
      while length(s) < 80
        s = [s,fgetl(fid)];
      end
      AA(i,:) = s;
      i=i+1;
    else
      end
  end
end
fclose(fid);
[s1,s2]=size(AA);
% ************************************************************************
% E-values
Ea434=19706-29.3*CalT;
Ea620=34;
Eb434=3073;
Eb620=44327-70.6*CalT;
e1 = Ea620./Eb434; e2 = Eb620./Ea434; e3 = Eb434./Ea434;
% **************************************************************************

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DRef1(i)=hex2dec(AA(i,15:18));  % Dark Reference LED
DSig1(i)=hex2dec(AA(i,19:22));  % Dark Signal LED
R434(i)=hex2dec(AA(i,23:26));  % 434nm Reference LED intensity
S434(i)=hex2dec(AA(i,27:30));  % 434nm Signal LED intensity
R620(i)=hex2dec(AA(i,31:34));  % 620nm Reference LED intensity
S620(i)=hex2dec(AA(i,35:38));  % 620nm Signal LED intensity
Ratio434(i)=hex2dec(AA(i,39:42)); % 434nm Ratio
Ratio620(i)=hex2dec(AA(i,43:46)); % 620nm Ratio
Batt(i)=hex2dec(AA(i,71:74));     % Battery voltage
Therm(i)=hex2dec(AA(i,75:78));    % Thermistor raw value
end

% Find first blank (SAMI-CO2's should always start with a blank)
[cx,y]=find(Type==5);
x1=cx(1);
A434Bk(1)=-log10(Ratio434(x1));
A620Bk(1)=-log10(Ratio620(x1));

% Blanks are set to run every 3.5 days
for i =1:s1
  if Type(1,i)==5
    A434Bka(k)=-log10(Ratio434(i)/16384);
    A620Bka(k)=-log10(Ratio620(i)/16384);
    blanktime(k)=(Time(i)/(60*60*24));
    datetime1(i)=(Time(i)/(60*60*24));
    Rt(i)=(Therm(i)/(4096-Therm(i)))*17400;
    InvT(i)=0.0010183+0.000241*(log(Rt(i)))+0.00000015*(log(Rt(i)))^3;
    TempK(i)=1/InvT(i);
    TempC(i)=TempK(i)-273.15;
    TempF(i)=1.8*TempC(i)+32;
    k = k+1;
  end
end

i2=1;
for i=1:s1
  if Type(1,i)==5 % Blank measurement
    if i2==1
      i2=i2+1;
    else
      A434Bk = A434Bka(i2);
      A620Bk = A620Bka(i2);
      i2=i2+1;
    end
    PCO2(i)=0;
  else if Type(i)==4 % CO2 measurement
    k434(i)=A434Bk;
    k620(i)=A620Bk;
    A434(:,i)=log10(Ratio434(:,i)/k434(i)); % 434 absorbance
    A620(:,i)=log10(Ratio620(:,i)/k620(i)); % 620 absorbance
    Ratio(:,i)=(A620(:,i))./(A434(:,i)); % Absorbance ratio
    datetime1(i)=(Time(i)/(60*60*24));
    % ******** Thermistor calculations ********
    Rt(i)=(Therm(i)/(4096-Therm(i)))*17400;
    InvT(i)=0.0010183+0.000241*(log(Rt(i)))+0.00000015*(log(Rt(i)))^3;
    TempK(i)=1/InvT(i);
    TempC(i)=TempK(i)-273.15;
    TempF(i)=1.8*TempC(i)+32;
    k1=0;
    RC021(i)=1*log10(V1(i).^2/V2(i));
    RC022(i)=(TempC(i)-CalT).*0.007+RC021(i);
    Tcoeff(i)=(0.0075778)-(0.0012389.*RC022(i)-(0.00048757.*RC022(i).^2);
    Tcor_RCO2(i)= RC021(i)+Tcoeff(i).*(TempC(i)-CalT);
Data Product Specification for Partial Pressure of CO2 in Seawater

PCO2(i) = 10.^(((-1*CalB)+((CalB^2)-(4*CalA*(CalC-Tcor_RCO2(i))))).^0.5)./(2*CalA));

i=i+1;
else
end
end

% Output text file
fid = fopen(outfile,'w');
fprintf(fid,'Time Type Temp pCO2
');
fmt = '%8.4f %8.4f %8.4f %8.4f
';
data=[datetime1; Type; TempC; PCO2];
fprintf(fid,fmt,data);
fclose(fid);
Appendix B  Output Accuracy

The Sunburst SAMI-CO2 instrument specifications indicate an accuracy of ±3 µatm, and a precision of <1 µatm (at standard temperatures and pressures).

Listed below are the DOORS requirements for accuracy and precision:

L4-CG-IP-RQ-505  pCO2 water instruments shall have an accuracy of ±4 µatm for concentrations ≤400 µatm.

L4-CG-IP-RQ-506  pCO2 water instruments shall have an accuracy of ±1% for concentrations > 400 µatm.

L4-CG-IP-RQ-507  pCO2 water instruments should have an accuracy of ±2 µatm for concentrations ≤400 µatm.

L4-CG-IP-RQ-508  pCO2 water instruments should have an accuracy of ±0.5% for concentrations > 400 µatm.

L4-CG-IP-RQ-509  pCO2 water instruments shall have a precision of ±2 µatm for concentrations ≤400 µatm.

L4-CG-IP-RQ-510  pCO2 water instruments shall have a precision of ±0.5% for concentrations > 400 µatm.

L4-CG-IP-RQ-511  pCO2 water instruments should have a precision of ±1 µatm for concentrations ≤400 µatm.

L4-CG-IP-RQ-512  pCO2 water instruments should have a precision of ±0.25% for concentrations > 400 µatm.

Appendix C  Sensor Calibration Effects

N/A