OCEAN OBSERVATORIES INITIATIVE

DATA PRODUCT SPECIFICATION FOR PARTIAL PRESSURE OF CO_2 IN SEAWATER

Version 1-00
Document Control Number 1341-00490
2012-06-18

Consortium for Ocean Leadership
1201 New York Ave NW, 4th Floor, Washington DC 20005
www.OceanLeadership.org

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

Version	Date	Description	Author
0-01	2012-04-19	Initial Draft	M. Vardaro
0-02	2012-04-27	Revisions from focused review	M. Vardaro
0-03	2012-05-30	Revisions from 5-day review	M. Vardaro
0-04	2012-06-05	Updated section 2.2.7	S. Webster
1-00	2012-06-15	Initial Release	E. Chapman

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

Table of Contents

1 Abstract

This document describes the procedure used to obtain the OOI Level 1 Partial Pressure of CO_2 (pCO_2) in Seawater data product, which is calculated using the output from the Sunburst $SAMI^2$-CO_2. 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 CO_2 in seawater

2.2.2 Data Product Abstract (for Metadata)

The pCO_2 data product PCO2WAT is the partial pressure of CO_2 in seawater, which is the pressure that would be exerted by CO_2 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. pCO_2 in the ocean is determined by measuring the amounts of dissolved CO_2 and HCO_3, 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 CO_2 in Seawater core data product is computed internally using calibration constants and the temperature-corrected CO_2 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

- pCO_2

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 CO_2 in atmosphere and surface seawater respectively.

2.3 Instruments

For information on the instruments from which the L1 Partial pressure of CO_2 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 $SAMI^2$-CO_2 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/$SAMI^2$-CO_2

(see DPS Artifacts >> CO2 MANUAL SAMI AFT combined.pdf)

SAMI Record Format Documentation

(see DPS Artifacts >> SAMI_Record_Format.pdf)

DeGrandpre, M.D., Baehr, M.M., & Hammar, T.R. (1999) Calibration-Free Optical Chemical Sensors. *Analytical Chemistry*, 71, 1152-1159.

(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 $SAMI^2$-CO_2

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 620nm wavelengths of light, provided by the manufacturer in written and digital form after every calibration or refurbishment cycle.

$Tcor\_RCO_2$ =	the temperature-corrected CO_2 measurement made using onboard measurements of temperature and optical absorbance
RCO_21 =	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 (RCO_21) at calibration temperatures
TempC =	Temperature in °C, derived from the thermistor raw value (Therm)

Type	=	Data Type (4 = Measurement, 5 = Blank)
DRef1	=	Dark Reference LED
DSig1	=	Dark Signal LED
R434	=	434nm Reference LED intensity
S434	=	434nm Signal LED intensity
R620	=	620nm Reference LED intensity
S620	=	434nm Signal LED intensity
Ratio434	=	434nm Ratio
Ratio620	=	620nm Ratio
Batt	=	Battery voltage
Therm	=	Thermistor raw value

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 pCO2 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$1 + 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^2-CO_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*^{2}-CO_2 instrument has two types of records, the regular measurement (type 4) and the blank measurement records (type 5), which contain the following variables:

```
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^2*-*CO_2 *record*:

*5B2704C8EF9FC90FE606400FE8063C0FE30674640B1B1F0FE6065A0FE9067F0FE
306A60CDE0FFF3B

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, Ea620, 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
*7E2705CBACEE7F007D007D0B2A00BF080500E00187034A008200790B2D00BE080600DE0
C1406C98C
*7E2704CBACEECB008000880B2900B2080600D300FB0263007F00890B2B00B4080700CE0C
5106C884
*7E2704CBACEF43007E00890B2701440807018904 5B0875007E00870B2B0140080201860C5
506C601
*7E2704CBACEFBB007E00820B2A042B0803051F1618278500800085 0B2A043C080405390C5
506C5A9
*7E2704CBACF033007F00840B28054D080606831CCC330A007F00850B290551080406800C5
606C556
*7E2704CBACF0AB007E00770B2804DE080605F31A672E9F008100790B2F04E0080705F70C
5606C5EB
*7E2704CBACF1230081007C0B2B00BF080800DB01BF0390007C00790B3000C7080B00EA0C
5606C80A
*7E2704CBACF19B008000750B2B01D20807023008310E94007E00730B2A01D2080502290C5
706C0A2
*7E2704CBACF213008000740B2A01D50808042F08501FC6007D00780B3201D8080A04350C5
706C0A5
*7E2704CBACF28B007F00710B2F0174080203570615189B008100730B2A0174080A03580C5
706C125
*7E2704CBACF303007E006B0B2C019B080803CC07001CBA007F006F0B300199080803D00C
5706C4E3

Test Data Output:

Time (Serial Format)	Real Date and Time	Data Type	Temperature (°C)	pCO2
39549.8622	4/12/12 20:41:34	5	18.8526	0
39549.8631	4/12/12 20:42:52	4	18.8765	294.172
39549.8645	4/12/12 20:44:53	4	18.9245	311.3361
39549.8659	4/12/12 20:46:54	4	18.9485	319.0101
39549.8673	4/12/12 20:48:55	4	18.9485	319.8925
39549.8686	4/12/12 20:50:47	4	18.9485	319.895
39549.87	4/12/12 20:52:48	4	18.8765	305.8104
39549.8714	4/12/12 20:54:49	4	19.0686	317.9661
39549.8728	4/12/12 20:56:50	4	19.0686	284.3676
39549.8742	4/12/12 20:58:51	4	19.0446	280.2324
39549.8756	4/12/12 21:00:52	4	18.9725	280.0354

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');

% 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))==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

fclose(fid);
[s1,s2]=size(AA);
% ************************************************************************
% E-values
Ea434=19706-29.3*CalT;
Ea620=34;
Eb434=3073;
Eb620=44327-70.6*CalT;
e1 = Ea620./Ea434; e2 = Eb620./Ea434; e3 = Eb434./Ea434;
% ************************************************************************
% Extract data from hex string
for i=1:s1
   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 Signal LED intensity
    R620(i)=hex2dec(AA(i,31:34));   % 620nm Reference LED intensity
    S620(i)=hex2dec(AA(i,35:38));   % 434nm Signal 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;
        V1(i)=Ratio(:,i)-e1;
        V2(i)=e2-e3.*Ratio(:,i);
        RCO21(i)=-1*log10(V1(i)./V2(i));
        RCO22(i)=(TempC(i)-CalT).*0.007+RCO21(i);
        Tcoeff(i)=(0.0075778)-(0.0012389.*RCO22(i))-(0.00048757.*RCO22(i).^2);
        Tcor_RCO2(i)= RCO21(i)+Tcoeff(i).*(TempC(i)-CalT);
```

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

% Output text file
fid = fopen(outfile,'w');
fprintf(fid,'Time \t Type \t Temp \t pCO2 \r\n');
fmt = '%8.4f \t %8.4f \t %8.4f \t %8.4f \r\n';
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