DATA PRODUCT SPECIFICATION FOR PARTIAL PRESSURE OF CO_2 IN SEAWATER

Version 2-00
Document Control Number 1341-00490
2030-02-25

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
2-00	2018-02-25	Revised section 4.6 to include updated test data set and output; revised Appendix A to reflect updated vendor-supplied equations [ECR-319]	W. Ruef

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 help@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
https://oceanobservatories.org/instruments/
for specifics of instrument locations and platforms.

2.4 Literature and Reference Documents

Sunburst Operating Manual AFT/$SAMI^2$-CO_2

(see OOI > Reference Archive > Data Product Specification Artifacts > 1341-00490_PCO2WAT > CO2 MANUAL SAMI AFT combined.pdf)

SAMI Record Format Documentation

(see OOI > Reference Archive > Data Product Specification Artifacts > 1341-00490_PCO2WAT > 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 OOI > Reference Archive > Data Product Specification Artifacts > 1341-00490_PCO2WAT > 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
BTB = Bromothymol blue, pH indicator used in 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.

e1, e2, e3 = equilibration constants for the BTB indicator solution at 434nm and 620nm wavelengths of light provided by the vendor based on lab determinations done with a single batch of BTB; constants are not currently recalculated when new batches of BTB are used. Constants are provided only in the context of the vendor's Matlab code and are not included as part of the calibration documentation package provided after each instrument calibration or refurbishment cycle. Communication with the vendor indicates future revisions to these constants are possible.

*** Note: these variables were previously calculated in the algorithm using inputs of Ea434, Eb434, Ea620, Eb620, which are no longer provided. ***

Tcor_RCO_2 = the temperature-corrected CO_2 measurement made using onboard measurements of temperature and optical absorbance
RCO_2 = 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_2) 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:

$$pCO_2 = 10\hat{}(((-1*CalB) + ((CalB\hat{}2) - (4*CalA*(CalC - Tcor\_RCO_2)))\hat{}0.5) / (2*CalA))$$

The calibration coefficients (CalT, CalA, CalB, and CalC), unique to each instrument and each calibration, are provided by the manufacturer.

"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

After careful review, the original data product algorithm (pco2_pco2wat) for this sensor was found to contain an error that resulted in calculation of incorrect derived L1 pCO2 values. In consultation with the vendor, the algorithm was corrected and verified. The updated example code from the vendor is contained in Appendix A, and the updated OOI algorithm code is available at https://github.com/oceanobservatories/ion-functions/blob/master/ion_functions/data/co2_functions.py.

4 Implementation

4.1 Overview

The included Matlab code (provided by R. Spaulding 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.

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)
- 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:

*BC2705D5A7C0E10082005A0CA9090E07CB08E82DCA4B1C0082005A0CA9090E07CD08EC0C3208C38A
*BC2704D5A7E2B1007E005A0CB1022F07C40443099F226D007F005A0CAF022F07C404400C3F08BE2E
*BC2704D5A7FEC90080005A0CAD028707CC03160B711800008300580CAC028607CC03160C4007389C
*BC2704D5A8006F0083005B0CA1028D07DE02F70BA016AF0081005A0CA2028D07E202F70C4007A16D
*BC2704D5A802150080005A0C98028D07E902DE0BAE15BF0081005A0C98028E07EB02DF0C40080C6B
*BC2704D5A803BB007F00590C98028307EB02EA0B6B161B008100580C94028107EE02EB0C41085372
*BC2704D5A80560007F005A0C9A027407E403050B26171F0083005C0C99027607E903060C4008862B
*BC2704D5A80707007F005A0CA0027007DE03210AF9182A008000590CA0026D07DE03240C400895E4
*BC2704D5A808AD0082005B0CA2026607D203470AC019A00080005C0CA6026607D403490C3F0899FF
*BC2704D5A80A54007F00560CAB025407CC03860A701BCF0083005C0CAA025707D003840C3F089BE2
*BC2704D5A80BF90080005A0CB3024907C603B60A2D1D99008100580CAF024707C603B90C3F089C58
*BC2704D5A80E140080005B0CB3023807C0041009CA20C40082005A0CB3023807C004110C3F08A0D4
*BC2704D5A8102F007F00580CB9022D07BA04350999222D0080005A0CB4022E07BC04370C3E08B067
*BC2704D5A812E70081005B0CBE022107B00479094A24AD0080005A0CBC022007B8047B0C3E08CEE4

Test Data Output:

Time	pCO2	Temp	BattV	DarkRef	DarkSig	Ratio434	Ref434	Sig434	Ratio620	Ref620	Sig620
42949.7419	0	7.3151	11.43	130	90	11722	3241	2318	19228	1995	2280
42949.842	609.8626	7.4258	11.48	126	90	2463	3249	559	8813	1988	1091
42949.9253	394.3221	16.2306	11.48	128	90	2929	3245	647	6144	1996	790
42949.9302	351.6737	13.8108	11.48	131	91	2976	3233	653	5807	2014	759
42949.9351	321.4986	11.39	11.48	128	90	2990	3224	653	5567	2025	734
42949.9399	324.067	9.8019	11.49	127	89	2923	3224	643	5659	2027	746
42949.9448	339.4317	8.6674	11.48	127	90	2854	3226	628	5919	2020	773
42949.9497	358.3335	8.3345	11.48	127	90	2809	3232	624	6186	2014	801
42949.9546	388.1735	8.2458	11.48	130	91	2752	3234	614	6560	2002	839
42949.9595	436.8431	8.2014	11.48	127	86	2672	3243	596	7119	1996	902
42949.9644	481.1713	8.1792	11.48	128	90	2605	3251	585	7577	1990	950
42949.9706	566.8172	8.0905	11.48	128	91	2506	3251	568	8388	1984	1040
42949.9768	607.5355	7.7359	11.48	127	88	2457	3257	557	8749	1978	1077
42949.9849	685.8555	7.0716	11.48	129	91	2378	3262	545	9389	1968	1145

Appendix A Example Code

```
% This m-file reads raw data from Sunburst SAMI pCO2 data file and
% calculates pCO2.
% Code supplied by Reggie Spaulding at Sunburst Sensors in Feb 2018.
%
% Test data file was created from data collected during the deployment of
% sensor SN C0123 in July 2017.
%
% ***************************************************************************
clear all

%
% Sensor Specific Calibration coefficients for C0123, 2017
%
CalT=4.6539;
CalA=0.0422;
CalB=0.6761;
CalC=-1.5798;

% e's for calculating pCO2, constants provided by Sunburst based on lab
% determinations with BTB
e1=0.0043;
e2=2.136;
e3=0.2105;

File = 'testFile.txt';
fid = fopen(File);

% Read in SAMI hex data
i=1; j=1; k=1;
while 1
   s=fgetl(fid);
   if s == -1, break,end % indicates EOF
   if ~isempty(s)
      if (strcmpi('*',s(1:1))==1 && strcmpi('04',s(6:7))| strcmpi('05',s(6:7)))
         if (length(s) == 81)
            s = s(2:length(s));
            while length(s) < 80
               s = [s,fgetl(fid)];
            end
            AA(i,:)= s;
            i=i+1;
         end
      else
      end
   end
end
fclose(fid);
[d1,d2]=size(AA);
% ***************************************************************************
% Extract data from hex string
for i=1:d1
   Type(i)=hex2dec(AA(i,5:6));  % Type 4 - Measurement, Type 5 - Blank
   Time(i)=hex2dec(AA(i,7:14));  % Time
   t_SAMI(i) = ((Time(i)/86400) +(365.25*4)+(1));
   DarkRef(i)=hex2dec(AA(i,15:18));  % Dark Reference LED
   DarkSig(i)=hex2dec(AA(i,19:22)); % Dark Signal LED
   Ref434(i)=hex2dec(AA(i,23:26));  % 434nm Reference LED intensity
   Sig434(i)=hex2dec(AA(i,27:30));  % 434nm Signal Signal LED intensity
   Ref620(i)=hex2dec(AA(i,31:34));  % 620nm Reference LED intensity
   Sig620(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
   Battery(i)=hex2dec(AA(i,71:74)); % Raw Battery Value
   BattV(i) = Battery(i)*15/4096; % Battery voltage
   Therm(i)=hex2dec(AA(i,75:78)); % Thermistor raw value
```

```
end

k=1;
for i=1:d1
    BFlag(i)=nan;
    if Type(i)==5 % Blank measurement
        A434Bka(k)=Ratio434(i)/16384;
        A620Bka(k)=Ratio620(i)/16384;
        blanktime(k)=((Time(i))/(60*60*24)); % Time of blank
        datetime1(i)=(Time(i)/(60*60*24));   % Time total
        Tc_SAMI(i)=(1./((0.0010183)+(0.000241.*log((Therm(i)./...
            (4096-Therm(i))).*17400))+((0.00000015.*log((Therm(i)./...
            (4096-Therm(i))).*17400).^3))))-273.15; % Temp
        k=k+1;
    end
end

% PCO2 Calculations
i2=1;
for i=1:d1
    if Type(i)==5
        A434Bk=A434Bka(i2);
        A620Bk=A620Bka(i2);
        calcCO2_1(i)=0;
        i2=i2+1;
    else if Type(i)==4
            k434(i)=A434Bk;
            k620(i)=A620Bk;
            A434(:,i)=-log10((Ratio434(i)./16384)/k434(i));
            A620(:,i)=-log10((Ratio620(i)./16384)/k620(i));
            Ratio(:,i)=(A620(:,i))/(A434(:,i));
            datetime1(i)=(Time(i)./(60*60*24));
            Tc_SAMI(i)=(1./((0.0010183)+(0.000241.*log((Therm(i)./...
                (4096-Therm(i))).*17400))+((0.00000015.*log((Therm(i)./...
                (4096-Therm(i))).*17400).^3))))-273.15; % Temp
            RCO2(:,i) = -log10((Ratio(:,i)-e1)./(e2-e3.*Ratio(:,i)));
            Tcor_RCO2i(:,i) = RCO2(:,i)+(0.008.*(Tc_SAMI(i)-CalT));
            Tcoeff(:,i) = (0.0075778)-(0.0012389.*Tcor_RCO2i(:,i))-...
                (0.00048757.*Tcor_RCO2i(:,i).^2);
            Tcor_RCO2(:,i) = RCO2(:,i)+(Tcoeff(:,i)).*(Tc_SAMI(i)-CalT);
            calcCO2_1(:,i) = (10.^(((-1*CalB)+((CalB^2)-(4*CalA.*...
                (CalC-Tcor_RCO2(:,i)))).^0.5)./(2*CalA)));
        end
    end
end

% *************************** Write output file ***************************
outfile_CO2=strcat(File(1:end-4),'_out.xls');
col_header={'Time','pCO2','Temp','BattV','DarkRef','DarkSig',...
    'Ratio434','Ref434','Sig434','Ratio620','Ref620','Sig620'};
datafinal_CO2=[t_SAMI;calcCO2_1;Tc_SAMI;BattV;DarkRef;DarkSig...
    ;Ratio434;Ref434;Sig434;Ratio620;Ref620;Sig620];
fid = fopen(outfile_CO2,'w');
fprintf(fid,['Time\t pCO2\t Temp\t BattV\t DarkRef\t DarkSig\t'...
    'Ratio434\t Ref434\t Sig434\t Ratio620\t Ref620\t Sig620\r\n']);
fmt = ['%8.4f \t %8.4f \t %8.4f \t %8.2f \t %8f \t %8f \t %8f \t'...
    '%8f \t %8f \t %8f \t %8f \t %8f \r\n'];
fprintf(fid,fmt,datafinal_CO2);
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