

Precision Gas System Isotope Analyzer (PGSISO) Instrument Handbook

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Acronyms and Abbreviations

| | |
|--------|--|
| ARM | Atmospheric Radiation Measurement |
| ASCII | American Standard Code for Information Interchange |
| CCL | Central Calibration Laboratory |
| CSV | comma-separated values |
| DQR | Data Quality Report |
| FTIR | Fourier Transform Infrared technique of trace gas measurement |
| HITRAN | high-resolution transmission molecular absorption line parameters database |
| IR | infrared |
| MALT | Multiple Atmospheric Layer Transmission to compute spectra |
| MCT | mercury-cadmium-telluride |
| PGSISO | precise gas system for isotopes |
| PPB | parts per billion |
| PPM | parts per million |
| QA | quality assurance (data) |
| QC | quality control/checks (data) |
| SGP | Southern Great Plains |
| VPDB | Vienna Pee Dee Belemnite standard for carbon and oxygen isotopic analysis |
| WMO | World Meteorological Organization |

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1.0 Instrument Title

Precision gas system isotope analyzer (PGSISO)

2.0 Mentor Contact Information

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3.0 Instrument Design

The PGSISO is a combination of several systems in series; (1) gas processing components that pressurize and prevent liquid water entering the sample stream, and (2) the Spectronus FTIR spectrometer, which measures continuous CO₂, ¹²CO₂, ¹³CO₂, CH₄, CO, N₂O, and H₂O. The Spectronus analyzer has been developed by the Centre for Atmospheric Chemistry at the University of Wollongong, Australia, and manufactured by Ecotech Pty Ltd, headquartered in Melbourne, Australia.

Operating parameters internal to the Spectronus are monitored and logged. Tower sample heights at 2m, 4m, 25m, and 60m above ground level, or calibration stream, is selected via Valco multi-port valve, and data are logged by the native Spectronus software. The Spectronus database file is converted to ascii format and further processed post-ingest to form the pgsiso.b1 datastream.

3.1 Instrument/Masurement Theory

The Spectronus FTIR Trace Gas Analyzer is used to determine simultaneously the concentrations of several trace gases in air or another gas stream by collecting and analyzing the Fourier Transform Infrared (FTIR) spectrum of the gas sample. In the closed-path trace gas analyzer the air is contained in a sample cell that is multi-passed by the IR beam. The analyzer consists of separate subsystems controlled by a single computer program:

- The sample handling subsystem, which carries out all sample handling, inlet sample stream selection, cell evacuation, and flushing procedures. This includes a 12-channel digital IO switching capability for switching 12 (or optionally more) solenoid valves, and also an 8-channel analogue-digital converter for logging environmental variables such as temperatures, pressures, and flows.
- The FTIR spectrometer, which produces and records the interferogram and then performs Fourier Transformation in order to obtain the infrared spectrum of sampled air. This spectrometer is a Bruker infrared (IR) cube fitted with a thermoelectrically cooled MCT (mercury-cadmium-telluride) detector (wavenumber range 1500-7800 cm^{-1}). The IR cube is coupled to a 24-meter multi-pass gas cell that contains the air to be analyzed.
- The spectrum analyzer, which provides quantitative analysis of measured spectra immediately after collection, with real-time display.
- Logging of analyzed concentrations, analysis parameters, and analogue input quantities to a comma-separated values (CSV) text file.

Optical techniques such as FTIR spectrometry determine the absolute concentrations of individual trace gas species from the quantitative analysis of selected absorption bands or lines in the measured spectrum. The FTIR spectrometer records a broadband mid-IR spectrum that can be analyzed in selected spectral regions for several trace gases. For CH_4 , CO , N_2O , and CO_2 combination bands near 3600 cm^{-1} , the low-resolution FTIR spectrometer does not resolve individual isotopic species, and the relevant whole absorption bands are fitted assuming that all isotopologues are present in natural abundance.

For these determinations natural variations in isotopic abundances do not significantly affect the FTIR measurements. In some cases, such as for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ analyzed in the ν_3 bands near 2300 cm^{-1} , individual isotopologue concentrations can be determined independently from the spectrum, allowing the calculation of isotopic ratios.

The quantitative analysis of measured IR absorption spectra uses a computational approach to best-fit regions of the measured spectrum with a calculated spectrum based on knowledge of the sample conditions (pressure, temperature, pathlength), the HITRAN database of spectral line parameters (Rothman et al. 2005, 2009) and a model of the FTIR instrument line shape. Trace gas concentrations and instrument parameters are iteratively adjusted in the calculation to achieve best fit. This approach uses the program MALT (Multiple Atmospheric Layer Transmission; Griffith 1996) to calculate spectra and is described in more detail in Griffith (2012) and the MALT user's manual.

From each measured spectrum, MALT retrieves the concentration of each target gas and converts to a mole-fraction scale using the measured total pressure and temperature of the sample. The raw FTIR scale depends on the accuracy of HITRAN parameters, the MALT spectrum model, the optical pathlength, temperature, pressure and other parameters. It is usually within a few percent of established standard reference scales (Smith 2011).

3.2 Instrument System Functional Diagram

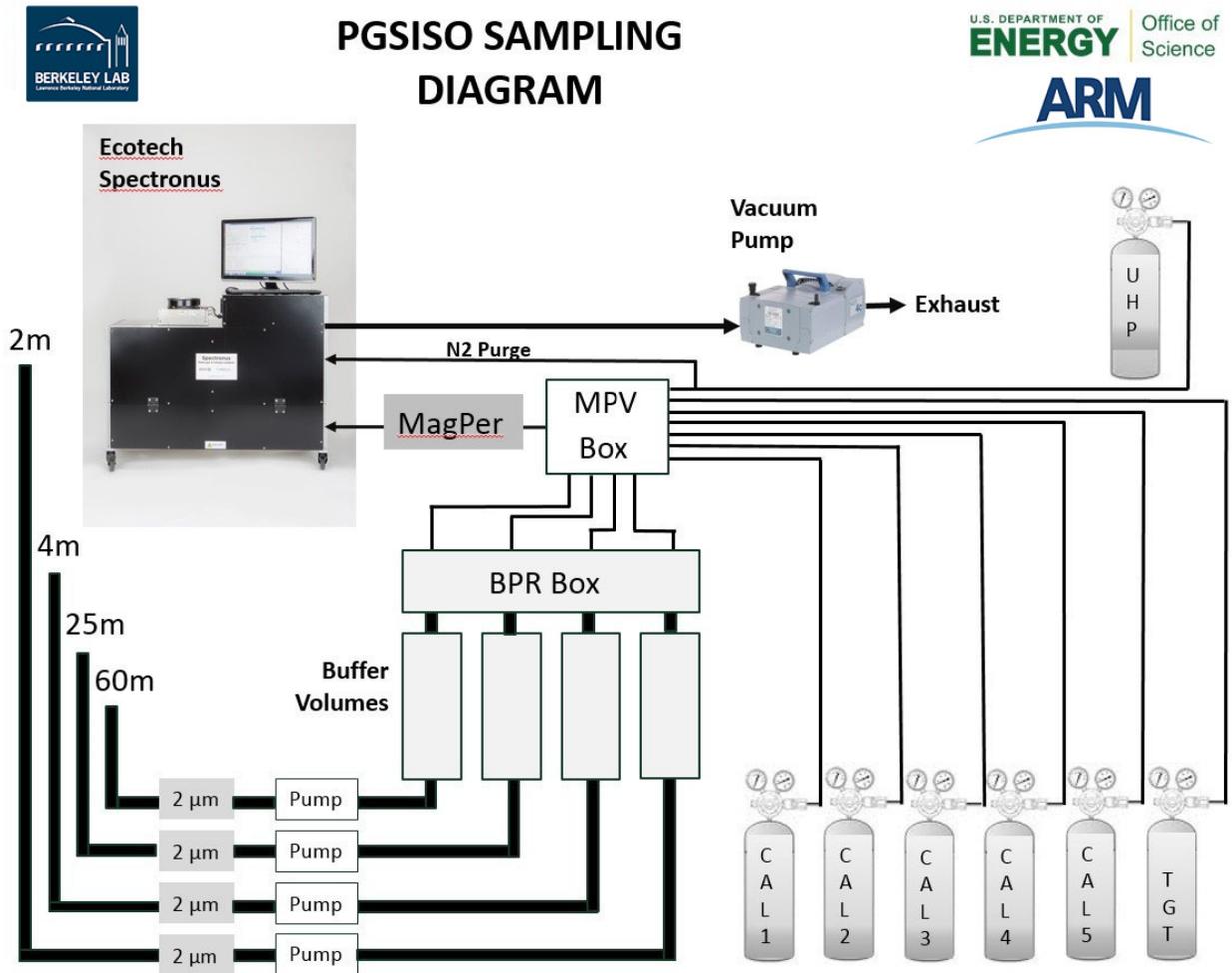


Figure 1. Plumbing diagram for PGSISO.

3.3 Calibration

Measurements of species are calibrated by measuring four span cylinders about every seven days, with measurements of one Target cylinder at the same pace, and another once per day. Linearly interpolated gain and offset coefficients for each species are applied to the sample data that undergo several stages of corrections prior to calibration. Notable regimes for reference calibration are:

- Aug 2013 deployment to Sep 2015 – 3-point calibration
- Sep 2015 to present – 4-point calibration.

Below are conversion and calibration steps included in the b1-level ingest processing.

3.3.1 Corrections

H₂O Correction

Water vapor displacement correction must occur for all species measured. The H₂O correction goes as:

$$\chi' = \chi / (1 - q/10^6)$$

where χ is the concentration of current sample measurement of species CO₂, ¹²CO₂, ¹³CO₂, CH₄, CO, N₂O
 q is the concentration of H₂O at the coincident to measurement of χ .

Residual Correction

Correction for the presence of residual air sample from previous measurement is required, depending on whether the measurement cell is flushed or not flushed with current sample air prior to measurement of the current sample.

$$\chi' = [(\chi \times P_{\text{cell}}) - (\chi_{\text{prev}} \times P_{\text{resid}})] / (P_{\text{cell}} - P_{\text{resid}})$$

where χ is the H₂O corrected concentration of sample measurement of species CO₂, ¹²CO₂, ¹³CO₂, CH₄, CO, N₂O

χ_{prev} is the H₂O corrected concentration from previous adjacent sample measurement

P_{resid} is the residual pressure of sample from previous measurement

P_{cell} is the cell pressure of current sample measurement

How and whether the correction is applied are determined based on measurement modes operated throughout the key periods:

- Aug 2013 deployment to Sep 2015
 - Tower and Target tank (inlet 1-4, and 10, respectively)
 - $P_{\text{resid}} = P_{\text{evac2}} + 83.2 + 8.3 + 4.0$
 where P_{evac2} is the evacuated pressure of previous sample measurement
 - Cal tanks (inlet 5-9)
 - $P_{\text{resid}} = 4.0$
- Sep 2015 to Jan 2017
 - Tower (inlet 1-4)
 - $P_{\text{resid}} = P_{\text{evac2}} + 8.3 + 4.0$
 - Target and Cal tanks (inlet 5-9, 10, 16)
 - $P_{\text{resid}} = 4.0$
- Jan 2017 to present → No residual correction.

Cross-Sensitivity Correction

This stage is for converting data to standard conditions. To first order, water vapor interference and sample pressure and temperature effects on the spectrum are included in the MALT calculation and spectrum fit. However, due to small inaccuracies and uncertainties in the measured spectrum, HITRAN line parameters, the spectral model, and the measured temperature and pressure, small dependences of apparent (raw) measured mole fractions on these parameters may remain.

$$\chi' = \chi - [(d\chi dQ \times (Q - Q_0)) - [(d\chi dP \times (P - P_0)) - [(d\chi dT \times (T - T_0)) - [(d\chi dF \times (F - F_0)) - [(d\chi dCO_2 \times (C - C_0)]]]]]]$$

where χ is the H₂O corrected and if applicable, residual corrected concentration of sample measurement of species CO₂, ¹²CO₂, ¹³CO₂, CH₄, CO, N₂O

$d\chi d^*$ is the cross-sensitivity coefficient for the species

Q is the concentration of H₂O and $Q_0 = 0$

P is the cell pressure and $P_0 = 1000$
 T is the cell temperature and $T_0 = 30$
 F is the cell fill pressure and $F_0 = 1$
 C is the concentration of CO_2 and $C_0 = 400$.

Rescale CO_2 Isotope Measurements from HITRAN to VPDB

To allow for calculation of $\delta^{13}\text{C}$ on the Vienna Pee Dee Belemnite (VPDB) scale

$$^{12}\chi_{\text{vpdb}} = ^{12}\chi' \times 1.000181$$

$$^{13}\chi_{\text{vpdb}} = ^{13}\chi' \times 1.000216$$

where $^{12}\chi'$ and $^{13}\chi'$ are the H_2O corrected, residual corrected, cross-sensitivity corrected concentration of scaled mole fraction of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ calculated from the HITRAN scale, respectively.

3.3.2 Reference Calibration

Calibration coefficients are determined by linear regression against known values, calculating gain and offset coefficients for each species. The calibration goes in general as:

$$\chi' = (\chi - b) / a$$

where χ is the measured concentration of each species CO_2 , $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, CH_4 , CO , N_2O with all corrections from Section 3.3.1 applied

b is the offset coefficient

a is the gain coefficient.

Isotope Calibration

Known values of calibration cylinders are reported for $\delta^{13}\text{C}$ and CO_2 , while scaled mole-fraction values are reported by the analyzer as χ'_{626} and χ'_{636} as for $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ and $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ isotopes respectively. The steps to produce calibrated $\delta^{13}\text{C}$ values are:

1. Convert the reported known values of CO_2 , $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ into the scaled mole-fraction values for χ'_{626} and χ'_{636} as:

$$\chi'_{626} = \chi_{\text{co2}} / X$$

$$\chi'_{636} = (1 + \delta^{13}) \times \chi'_{626}$$

where χ_{co2} is the known mole fraction of CO_2

δ^{13} is shorthand for $\delta^{13}\text{C}/1000$, similarly for δ^{18} and δ^{17} using known values for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ respectively

X is the approximated sum of the dominant CO_2 isotopologues as:

$$X \approx X_{626} + [(1 + \delta^{13}) \times X_{636}] + [(1 + \delta^{18}) \times X_{628}] + [(1 + \delta^{17}) \times X_{627}] + X_{\text{rest}}$$

where δ^{17} is approximated as $0.5 \times \delta^{18}$ assuming mass dependence and since the value is not directly measured

and,

$$X_{\text{rest}} = 1 - (X_{626} + X_{636} + X_{628} + X_{627})$$

and the abundances:

X_{626} is the abundance of $^{16}\text{O}^{12}\text{C}^{16}\text{O}$

X_{636} is the abundance of $^{16}\text{O}^{13}\text{C}^{16}\text{O}$

X_{628} is the abundance of $^{16}\text{O}^{12}\text{C}^{18}\text{O}$

X_{627} is the abundance of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$.

2. Calculate gain and offset coefficients independently for χ'_{626} and χ'_{636} in the same manner as the other species.
3. Calculate calibrated $\delta^{13}\text{C}$ using calibrated scale mole-fraction values:

$$\delta^{13}\text{C} = [(\chi'_{636} / \chi'_{626}) - 1] \times 1000\text{‰}$$
 where in this case χ'_{626} and χ'_{636} are the measured and calibrated scaled mole fractions for $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ and $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ respectively, with all corrections from 3.3.1 applied.

3.4 Uncertainty

Overall instrument uncertainty is characterized by the variability in the calibration residual from measurements of target cylinders compared to the known secondary values of each species, across the record from October 2013 to present (as of the date of this handbook).

This allows for the uncertainty to encompass components of uncertainty that are caused by systematic and/or operational errors that may or may not be characterized and that come from the actual operation of the system.

3.4.1 Uncertainty from Calibration Residuals

The calibration residual is defined as: Residual = Measured – Known.

The table below represents uncertainty metrics used by mentors to assess instrument performance, where columns are defined as:

MEAN = mean of difference measured and known quantities as, $\chi_{\text{resid}} = \chi_{\text{meas}} - \chi_{\text{known}}$ where χ are the measured calibrated or known values of species CO_2 , $\delta^{13}\text{C}$, CH_4 , CO , and N_2O

STDERR = the standard error of the mean of residuals

RMSE = the root mean square error calculated as

$$\sqrt{(\sum \chi_{\text{resid}}^2 / N)}$$

where the summation occurs over the square of residual from of N Target tank measurements used in the assessment.

Table 1. Target calibration residual statistics on N measurements.

| | Target (MPV Port 10) | | | | Span Target (MPV Port 6) | | | |
|--------------------|----------------------|--------|------|-----|--------------------------|--------|------|-----|
| | MEAN | STDERR | RMSE | N | MEAN | STDERR | RMSE | N |
| CO2 (ppm) | -0.08 | 0.01 | 0.16 | 310 | -0.03 | < 0.01 | 0.06 | 206 |
| DELTA13C (per mil) | -0.06 | 0.01 | 0.17 | 312 | -0.03 | 0.01 | 0.13 | 208 |
| CH4 (ppb) | -0.16 | 0.02 | 0.33 | 310 | 0.01 | 0.01 | 0.19 | 207 |
| CO (ppb) | -0.47 | 0.04 | 0.89 | 311 | 0.29 | 0.02 | 0.37 | 207 |
| N2O (ppb) | 0.08 | 0.01 | 0.19 | 312 | -0.03 | 0.01 | 0.13 | 207 |

3.4.2 Culling Data for Residuals Statistics

Not all Target cylinder measurements are used in the assessment of instrument uncertainty. In addition to the diagnostic QC tests the measurements undergo (Section 4.2), specified periods of measurements of the Target or Span cylinders are excluded from statistics using machine-readable documentation describing possible or confirmed reasons for instrument instability coincident with those measurements. This machine-readable documentation is a mentor-complied .csv file of all of the Data Quality Reports (DQRs) associated with the datastream and is used as a configuration file in the data ingest process. Examples of criteria for manually identified periods of instrument instability include:

- If H₂O measurements are abnormally high or variable
- Gain or Offset calibration coefficient outliers or periods of systematic deviation from expected values; significant outliers suggest the instrument was not in optimal condition and may be coincident with the previous criteria.

For the case of coefficients, when data is being reprocessed and coefficients are recalculated; the QC state of coefficients corresponding to the DQR entries are overwritten as “missing value” to then be excluded from linear interpolation of coefficients.

4.0 Definitions and Relevant Information

The b1-level datastream is named as:
sgppgsisoC1.b1

Auxiliary and input datastream names associated with producing b1-level datastreams are:
sgppgsisoC1.a1
sgppgsisoC1.b0
sgppgsisocoeffC1.b1

4.1 Primary Variables

At b1 level primary variable names are:
CO2_AVG_CORR
CH4_AVG_CORR
CO_AVG_CORR
N2O_AVG_CORR
DELTA13C

Associated QC variables:
CO2_AVG_CORR_QC
CH4_AVG_CORR_QC
CO_AVG_CORR_QC
N2O_AVG_CORR_QC
DELTA13C_QC

Note:

- The “best data” are those with *_QC values that are any of (0, 8, 16, 24, 128) for tower or Target
- Tower sample data correspond to VALCOPOSITION equal to 1, 2, 3, or 4, as 2m, 4m, 25m, and 60m sample heights respectively.

4.2 QC Bit Definitions

```

flag_method = "bit" ;
bit_1_description = "Value is equal to missing_value -9999." ; 1
bit_2_description = "Value is less than the valid_min." ; 2
bit_3_description = "Value is greater than the valid_max." ; 4
bit_4_description = "Value for *_slope is missing value" ; 8
bit_5_description = "Value for *_slope_err is missing value" ; 16
bit_6_description = "Value for *_slope is below valid_min." ; 32
bit_7_description = "Value for *_slope is above valid_max." ; 64
bit_8_description = "Value for *_slope is significant with respect to a slope of zero, where
(abs(co2_slope-co2_slope_err) > 0)" ; 128
bit_9_description = "QC state for at least one of the mentor-defined auxiliary variables is not equal to 0" ;
256
bit_10_description = "Measurement follows a tank for which residual correction is not a sufficient
correction" ; 512
bit_11_description = "Measurement of N2 Purge Tank" ; 1024

```

4.3 Calibration Database

Calibration tank values are transcribed to a machine-readable configuration file used in Atmospheric Radiation Measurement (ARM) user facility ingest processing. The file is updated by the mentor each time the calibration tanks are changed out – about once every five years. The values are provided by the World Meteorological Organization (WMO)’s Central Calibration Laboratory (CCL) at the U.S. National Oceanic and Atmospheric Administration’s Earth System Research Laboratory. The calibration scales used for each of the species for current installed calibration cylinders (July 2018) are given below in Table 2.

Table 2. WMO CCL scale spans for each species.

| | Calibration Scale |
|------------------|-----------------------------|
| CO ₂ | WMO-CO ₂ -X2007 |
| CH ₄ | WMO-CH ₄ -X2004 |
| CO | WMO-CO-X2014 |
| N ₂ O | WMO-N ₂ O-X2006A |

Contact the mentor for access to calibration certificates of each species.

5.0 Citable References

Contact instrument mentors for up-to-date references.

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http://www.wmo.int/pages/prog/arep/gaw/documents/Final_GAW_213_web.pdf



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