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## **CCG-Flasks Instrument Handbook**

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# **CCG-Flasks Instrument Handbook**

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## Acronyms and Abbreviations

CCL	Central calibration laboratory
CH <sub>4</sub>	Methane
CO	Carbon monoxide
CO <sub>2</sub>	Carbon Dioxide
ESRL	Earth System Research Laboratory
GAW	Global Atmosphere Watch
GHG	Greenhouse Gas
H <sub>2</sub>	Hydrogen
INSTARR	Institute of Arctic and Alpine Research
LBNL	Lawrence Berkeley National Laboratory
NOAA	National Oceanic and Atmospheric Administration
N <sub>2</sub> O	Nitrous oxide
SF <sub>6</sub>	Sulfur hexafluoride
SGP	Southern Great Plains
SIL	Stable Isotope Laboratory
WMO	World Meteorological Organization

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## 1.0 Instrument Title

CCG-Flasks

## 2.0 Mentor Contact Information

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## 3.0 Vendor/Developer Contact Information

Surface measurements	Aircraft measurements	
		
Model Sherpa 70	Model Sherpa 90	Model Sherpa 80

### Surface-based sampling

Samples are collected from the one of the two 60m inlet in the PGS shed. A site technician triggers sampling, usually at 2pm local time, every Thursday. Each flask (2.5liters) is sampled for about 2 minutes and pressurized to 40 PSI. This system automatically purges the flasks, dries the air sample, and fills the flasks.

### Aircraft-based sampling

Samples are collected from the community inlet for as many as twelve elevations. The pilot triggers sampling when location and latitude have been reached. Each flask (0.75 liters) is sampled for about 2 minutes and pressurized to 40 PSI. The sampler has two components: (1) a rack mounted programmable compressor package (PCP, see picture below) and (2) a programmable flask package (PFP). Prior each flight, the pilot connects a new PFP to the PCP. An automatic test is then performed to check for leaks. After each flight the PFP is sent back to the laboratory for analysis of trace gases.

## 4.0 Instrument Description

Data from flasks are sampled at the Atmospheric Radiation Measurement Program (ARM), Southern Great Plains Site (SGP) and analyzed by the National Oceanic and Atmospheric Administration (NOAA), Earth System Research Laboratory (ESRL). The SGP site is included in the NOAA Cooperative Global Air Sampling Network. The surface samples are collected from a 60 m tower at the ARM SGP Central Facility, usually once per week in the afternoon around 2pm local time. The aircraft samples are collected approximately weekly from a chartered aircraft, and the collection flight path is centered over the tower where the surface samples are collected.

## 5.0 Measurements Taken

- CO<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O, H<sub>2</sub>, SF<sub>6</sub> mixing ratios

- Isotopic ratio data are expressed as deviations from an agreed-upon reference standard using the delta notation:  $\delta = (R_{\text{sample}}/R_{\text{reference}} - 1)$ , with  $R = [\text{heavy isotope}]/[\text{light isotope}]$ .  $\delta$ -Values are expressed in multiples of 0.001 (‰; per mil ‘units’).

Specifically  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotopic ratios for CO<sub>2</sub> and CH<sub>4</sub> are defined as:

$$\delta^{13}\text{C}_{\text{Sample}} = \left( \frac{^{13}\text{C}/^{12}\text{C}_{\text{Sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{PDB}}} - 1 \right) \cdot 1000$$

with respect to Pee Dee Belemnite (PDB) standard .

$$\delta^{18}\text{O} = \left( \frac{\left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left( \frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} - 1 \right) * 1000 \text{ ‰}$$

where the standard has a known isotopic composition, such as [Vienna Standard Mean Ocean Water](#) (VSMOW).

## 5.1 Data Object Description

Conventions: ARM-1.1

qc\_standards\_version: 1.0

reporting\_interval: 1 minute

reporting\_interval\_comment: The time assigned to each data point indicates the beginning of any period of averaging data.

## 5.2 Data Ordering

For ease of the use, the same data is grouped and presented by sampling method. All data measured from the 60 m tower is placed into the 'sgpccg.surface' file; all data from aircraft sampling is placed into the 'sgpccg.aircraft' file. The b1-level files for a calendar year are updated annually to c1-level files, based on recalibrations. When this update occurs (usually in midsummer of the following year), the previous b1 files should be discarded.

Note that these data sets could be used in conjunction with other carbon cycle datastreams: AOS, AOSGHG, PGS, and PGSISO datastreams. The surface flask collection is co-located at the 60 m tower with the PGS (Precision Gas System, continuous, precise CO<sub>2</sub> mixing ratio measurements at 2 m, 4 m, 25 m, and 60 m), and eddy covariance flux measurements (CO2FLX) at 4 m..

There are two file types:

- b1: data are reported in scientific units (mixing ratio for trace gases, per mil for isotopic ratios) edited to correct errors in dates, times, etc. These data are provisional and will most likely change when going to C1.
- c1: the b1 data have been further screened for errors, passed through a data selection process (more flags applied), and mixing or isotopic ratios have been recalculated if reference gases have been found to be drifting. The c1 data are essentially "final" values, except that we may occasionally reprocess the data, based on retrospective analyses of standards and working reference gases.

The data files contain one record for each atmospheric measurement of a single parameter or trace gas species. Fields are defined as follows:

Field 1: [SITE CODE] The three-character sampling location code (SGP).

Field 2: [YEAR] The sample collection date and time in UTC.

Field 3: [MONTH]

Field 4: [DAY]

Field 5: [HOUR]

Field 6: [MINUTE]

Field 7: [SECOND]

Field 8: [FLASK ID] The sample container ID.

Field 9: [METHOD] A single-character code that identifies the sample collection method. The codes are:

- P - Sample collected using a portable, battery powered pumping unit. Two flasks are connected in series, flushed with air, and then pressurized to 1.2 - 1.5 times ambient pressure.
- D - Similar to P but the air passes through a condenser cooled to about 5 deg C to partially dry the sample.
- G - Similar to D but with a gold-plated condenser.
- T - Evacuated flask filled by opening an O-ring sealed stopcock.
- S - Flasks filled by sampling air from the in situ measurement air intake system.
- F - Five liter evacuated flasks filled by opening a ground glass, greased stopcock.

Field 10: [LATITUDE] The latitude where the sample was collected.

Field 11: [LONGITUDE] The longitude where the sample was collected

Field 12: [ALTITUDE] The altitude of the sample inlet (masl).

Field 13: [EVENT NUMBER] A long integer that uniquely identifies the sampling event.



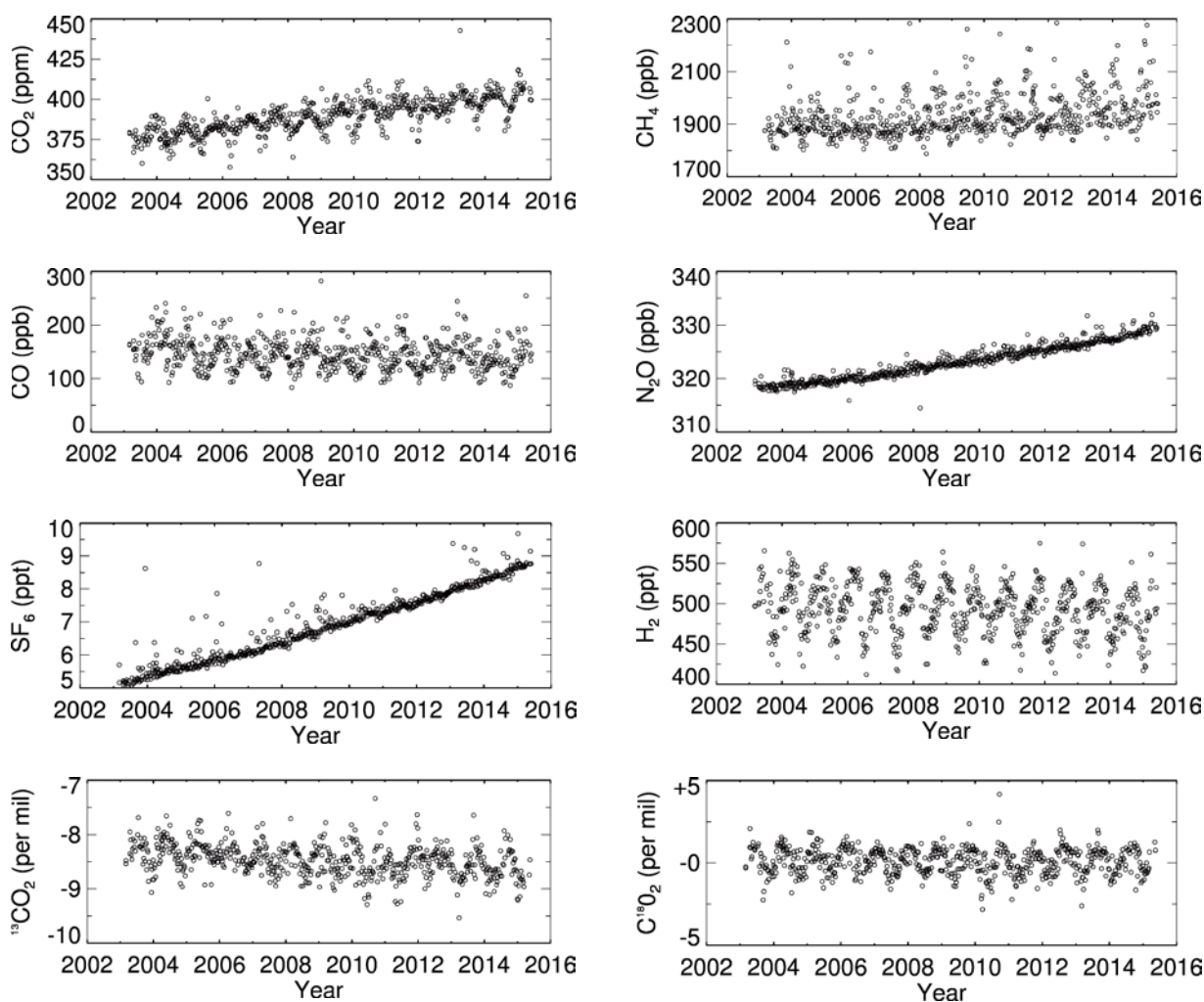
There is a group of 3 fields for each parameter and measurement group included in the file.

- Field ##+1: [TRACE GAS NAME] Gas identifier (e.g., co2, co2c13).
- Field ##+2: [MEASURED VALUE] Dry air mole fraction or isotopic composition. Missing values are denoted by -999.99.
- Field ##+3: [QC FLAG] A three-character field indicating the results of our data rejection and selection process, described in section 5.4.

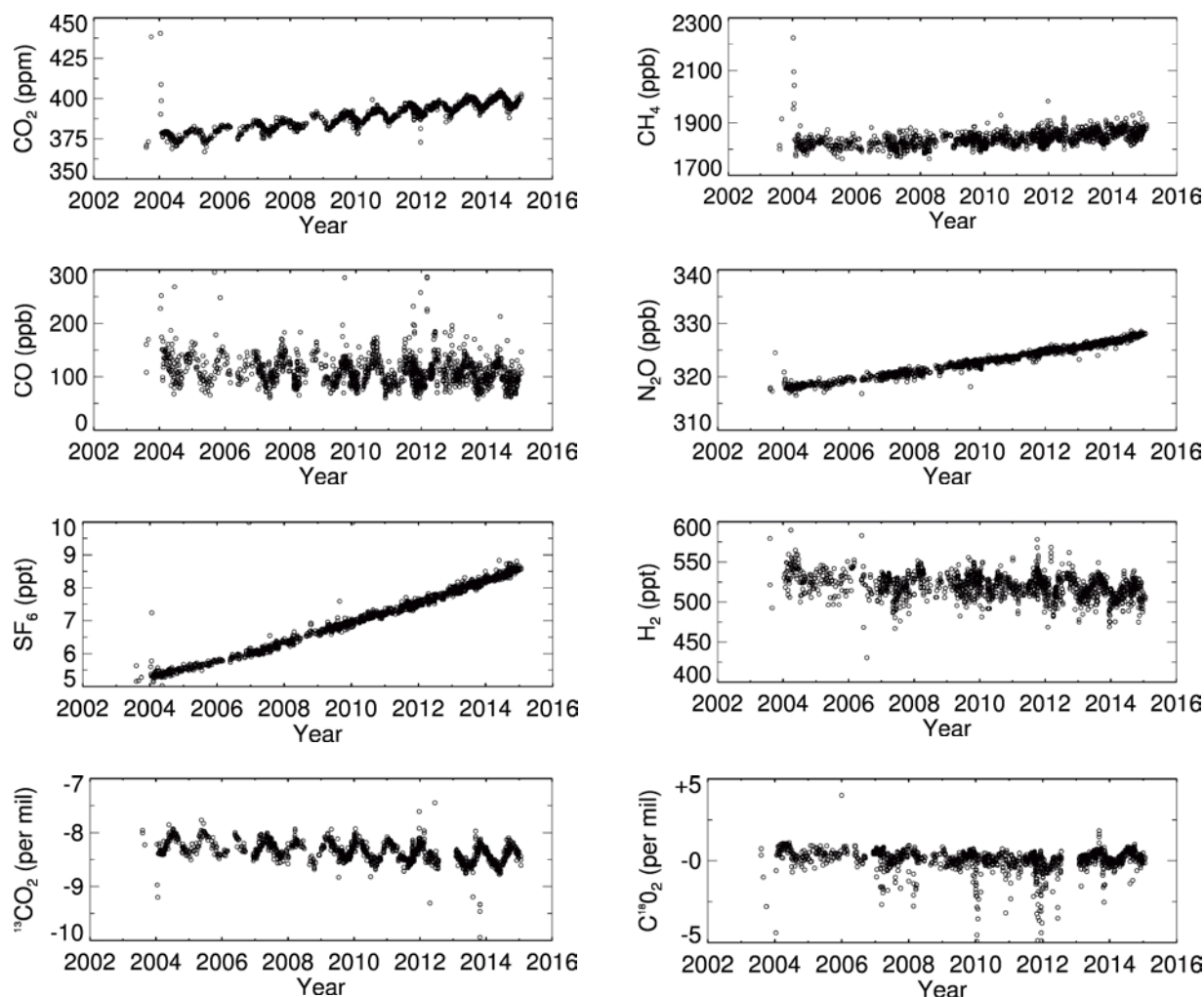
Fields in each line are delimited by whitespace.

## 5.3 Data Plots

### Surface-based observations



### Aircraft-based observations (example for sampling height at 3000m)



## 5.4 Data Quality

We use a 3-column quality control flag where each column is defined as follows:

column 1: REJECTION flag. An alphanumeric other than a period (.) in the FIRST column indicates a sample with obvious problems during collection or analysis. This measurement should not be interpreted.

column 2: SELECTION flag. An alphanumeric other than a period (.) in the SECOND column indicates a sample that is likely valid but does not meet selection criteria determined by the goals of a particular investigation.

column 3: INFORMATION flag. An alphanumeric other than a period (.) in the THIRD column provides additional information about the collection or analysis of the sample. WARNING: A "P" in the 3rd column of the QC flag indicates the measurement result is preliminary and has not yet been carefully examined by the PI. The "P" flag is removed once the quality of the measurement has been determined.

Samples are collected in pairs at the surface, and in the aircraft prior to 2006. The pair difference is calculated, and samples with a pair difference greater than 0.5 ppm ("bad pairs") are flagged. Through 1988 one or both members of a bad pair were sometimes retained if they fell within  $\pm 3$  residual standard deviations from a fitted curve. From 1989 to the present, both members of bad pairs have been automatically rejected. Retained and rejected flasks are flagged as follows:

	Flag	Description
RETAINED		
	...	(3 periods) good pair ( $D \leq 0.5$ ppm)
	..H	high member of bad pair; retained
	..L	low member of bad pair; retained
	..I	sample has also been measured by another lab as part of an intercomparison experiment
SELECTED		
	.X.	flagged automatically as an outlier, greater than 3 sigma from a fitted curve
	.Z.	flagged manually as an outlier (this is necessary to prevent distortion of the curve used for automated data selection)
REJECTED		
	+..	high member of bad pair; rejected
	-..	low member of bad pair; rejected
	*..	off scale or broken flask; rejected
	N..	rejected due to error in sampling or analysis
	A..	rejected due to error in analysis
	T..	sample collected as part of a methods test; not used in data analysis

## 5.5 Instrument Mentor Monthly Summary

The LBNL and NOAA teams produces automated data visualization and quality checking system, which includes an automated data quality checking routine. This is done on a monthly basis.

## 5.6 Calibration Data Base

CO<sub>2</sub>: The CO<sub>2</sub> mixing ratios reported in these files were measured using a nondispersive infrared absorption technique, and each aliquot is referenced to the WMO CO<sub>2</sub> standard scale

CH<sub>4</sub>: All samples are analyzed by gas chromatography with flame ionization detection, and each aliquot was referenced to the WMO CH<sub>4</sub> standard scale.

CO: All samples are analyzed using gas chromatography with mercuric oxide reduction detection, and all measurements are referenced to the WMO CO scale.

N<sub>2</sub>O: All samples were analyzed using gas chromatography with electron capture detection, and all measurements are referenced to the WMO N<sub>2</sub>O scale.

H<sub>2</sub>: All air samples are analyzed for H<sub>2</sub> using gas chromatography with mercuric oxide reduction detection, with all measurements referenced to an internal NOAA ESRL H<sub>2</sub> calibration scale.

SF<sub>6</sub>: All samples are analyzed for SF<sub>6</sub> using gas chromatography with electron capture detection, and all measurements are referenced to the NOAA ESRL SF<sub>6</sub> scale.

δ<sup>13</sup>C and δ<sup>18</sup>O for CO<sub>2</sub> and δ<sup>13</sup>C for CH<sub>4</sub>: The isotopic analyses were carried out at the INSTAAR Stable Isotope Laboratory at the U. of Colorado in Boulder and are referenced to the PDB and VSMOS standards.

## 6.0 Technical Specification

### 6.1 Units

Species	units
CO <sub>2</sub>	ppm
CH <sub>4</sub>	ppb
N <sub>2</sub> O	ppb
CO	ppb
SF <sub>6</sub>	ppt
H <sub>2</sub>	ppt
δ <sup>13</sup> C of CO <sub>2</sub>	‰
δ <sup>18</sup> O of CO <sub>2</sub>	‰
δ <sup>13</sup> C of CH <sub>4</sub>	‰

One per mil (‰) denotes one part per 1,000 parts, one part in 10<sup>3</sup>,  $1/1,000 \times 100\% = 0.1\%$  (or 1% = 10 per mil), and a value of  $1 \times 10^{-3}$ .

One part per million (ppm) denotes one part per 1,000,000 parts, one part in 10<sup>6</sup>,  $1/1,000,000 \times 100\% = 0.0001\%$  (or 1% = 10,000 ppm), and a value of  $1 \times 10^{-6}$ .

One part per billion (ppb) denotes one part per 1,000,000,000 parts, one part in 10<sup>9</sup>,  $1/1,000,000,000 \times 100\% = 0.0000001\%$  (or 1% = 10,000,000 ppb) and a value of  $1 \times 10^{-9}$ .

One part per trillion (ppt) denotes one part per 1,000,000,000,000 parts, one part in 10<sup>12</sup>, and a value of  $1 \times 10^{-12}$ .

### 6.2 Range

The optimum range of measurements is dictated by the range of primary calibration standard used for each species.

Species	range
CO <sub>2</sub>	250 – 520 ppm
CH <sub>4</sub>	300 -5,000 ppb

N <sub>2</sub> O	260 -370 ppb
CO	30 – 1000 ppb
SF <sub>6</sub>	2-20 ppt
H <sub>2</sub>	140 -1,200 ppt
δ <sup>13</sup> C of CO <sub>2</sub>	-7.5 to -9 per mil
δ <sup>18</sup> O of CO <sub>2</sub>	-2 to +2 per mil
δ <sup>13</sup> C of CH <sub>4</sub>	standardized isotopic calibration in development

### 6.3 Repeatability

The current WMO CO<sub>2</sub> Mole Fraction Scale consists of a set of 15 CO<sub>2</sub>-in-air primary standard calibration gases ranging in CO<sub>2</sub> mole fraction from 250 to 520 ppm CO<sub>2</sub> in dry air. The 15 WMO primary standards have been calibrated at regular intervals, between 1 and 2 years, by the ESRL manometric system. The uncertainty of the 15 primary standards was estimated to be 0.069 ppm (one-sigma). Manometric calibrations results indicate that there is no evidence of overall drift of the Primaries from 1996 to 2004. In order to lengthen the useful life of the Primary standards, ESRL has always transferred the scale via NDIR analyzers to the secondary standards. The mean reproducibility of NDIR transfer calibrations was about 0.03 ppm (two sigma) from 1979 to present.

The current WMO CH<sub>4</sub> Mole Fraction Scale consists of a set of 22 CH<sub>4</sub>-in-air primary standard calibration gases ranging in CH<sub>4</sub> mole fraction from 300 to 5900 ppb CH<sub>4</sub> in dry air. The uncertainty of the 22 primary standards was estimated to be 1 ppb.

The current WMO CO Mole Fraction Scale consists of a set of 14 CO-in-air primary standard calibration gases ranging in CO mole fraction from 300 to 1000 ppb CO in dry air. The uncertainty of the 14 primary standards was estimated to be 2.6 ppb.

The current N<sub>2</sub>O scale is based on 13 primary standards prepared by static gravimetric dilution from 99.9% pure N<sub>2</sub>O in 5.9-L aluminum cylinders. All standards contain CO<sub>2</sub> and SF<sub>6</sub> at near ambient levels. Assigned values were determined by fitting a 2nd order polynomial to the response of each standard (relative to a 318 ppb natural air secondary standard) measured using an HP6890 GC with electron capture detection. Analysis precision was typically less than 0.05% (one standard deviation). The standard deviation of residuals is 0.33 ppb.

The current H<sub>2</sub> scale is based on 13 primary standards of hydrogen in air ranging from 140 to 1200 ppb. The current scale is WMO H<sub>2</sub> X2009 (formerly the MPI-2009 H<sub>2</sub> scale). Recently a growing H<sub>2</sub> mole fraction in two of the primary standards has been detected. Experimental results suggest a bias of the scale of 2-3 ppb in the atmospheric range that will induce a revision of the WMO scale in the next scale.

The X2014 SF<sub>6</sub> scale is defined by 17 primary standards over the range 2-20 pmol mol<sup>-1</sup> (ppt), prepared by static gravimetric dilution in 5.9-L aluminum cylinders. Assigned values were determined by fitting a 2<sup>nd</sup> order polynomial to the response of each standard (relative to a 8.25 ppt natural air secondary

standard) measured using an HP6890 GC with electron capture detection (GC-ECD). Analysis repeatability (precision) was typically less than 0.3% (one standard deviation).

The stable isotopes of carbon and oxygen in CO<sub>2</sub> extracted from the standard cylinder air have been analyzed at the Stable Isotope Laboratory at CU-INSTAAR in Boulder, Colorado, using a Isoprime (Elementar Group) dual inlet isotope-ratio mass spectrometer. The details of these methodologies can be found in Troler et al. 1996, as well as: <http://instaar.colorado.edu/research/labs-groups/stable-isotope-laboratory/> and on the NOAA ESRL/GMD ftp data server: [ftp://ftp.cmdl.noaa.gov/ccg/co2c13/flask/README\\_flask\\_co2c13.html](ftp://ftp.cmdl.noaa.gov/ccg/co2c13/flask/README_flask_co2c13.html). For carbon and oxygen isotopes, the reference is VPDB-CO<sub>2</sub> (Coplen 1995). The current scale at SIL was set using NBS-19 and NBS-20 (carbonates) and VSMOW, GISP and SLAP (waters).

## 6.4 Input Voltage

Both systems are powered using 110-120V, at 50-60 Hz.

## 6.5 Input Current

Typical: 500 mA

Max: 2A

## 6.6 Input Values

N/A

## 6.7 Output Values

N/A

# 7.0 Setup and Operation of Instrument

Flask sampling is triggered manually by technician or pilot.

## 8.0 Calibration

WMO/GAW Central Calibration Laboratories (CCLs) currently exist for: carbon dioxide (CO<sub>2</sub>, at NOAA/ESRL), methane (CH<sub>4</sub>, at NOAA/ESRL), nitrous oxide (N<sub>2</sub>O, at NOAA/ESRL), carbon monoxide (CO, at NOAA/ESRL), sulphur hexafluoride (SF<sub>6</sub>, at NOAA/ESRL), stable isotopes in CO<sub>2</sub> (only for CO<sub>2</sub>-in-air measurements, at Max-Planck Institute for Biogeochemistry (MPI-BGC), and hydrogen (H<sub>2</sub>, at MPI-BGC). See Table below shows a list of current scales used.

Species	WMO scale currently used
CO <sub>2</sub>	X2007
CH <sub>4</sub>	X2004A
N <sub>2</sub> O	X2006A
CO	X2014A
SF <sub>6</sub>	X2014
H <sub>2</sub>	X2009
δ <sup>13</sup> C of CO <sub>2</sub>	VPDB-CO2
δ <sup>18</sup> O of CO <sub>2</sub>	VPDB-CO2
δ <sup>13</sup> C of CH <sub>4</sub>	TBD

Calibration results are based on analysis performed by the WMO/GAW Central Calibration Laboratories (CCL) located at the NOAA/ESRL. WMO/GAW mole fraction scales are developed and maintained by ESRL in their role as CCL. Results are traceable to the SI unit “amount of substance fraction”. Equipment used to develop mole fraction scales and establish traceability to the SI are traceable to national standards for mass, temperature, pressure, and amount of substance fraction (O<sub>2</sub> in N<sub>2</sub>). For more information on calibration scales and analysis methods, see <http://www.esrl.noaa.gov/gmd/ccl>.

## 9.0 Maintenance

Pumps diaphragm is replaced when needed.

## 10.0 Citable References

Biraud, S. C., Torn, M. S., Smith, J. R., Sweeney, C., Riley, W. J., and Tans, P. P.: A multiyear record of airborne CO<sub>2</sub> observations in the US Southern Great Plains, Atmos. Meas. Tech., 6, 751-763, doi:10.5194/amt-6-751-2013, 2013.

### CO<sub>2</sub> WMO Scale:

Zhao, C., and P.P. Tans (2006), Estimating uncertainty of the WMO Mole Fraction Scale for carbon dioxide in air, J. Geophys. Res. 111, D08S09, doi: 10.1029/2005JD006003.

Zhao, C., P.P. Tans and K.W. Thoning (1997), A high precision manometric system for absolute calibrations of CO<sub>2</sub> in dry air. Journal of Geophysical Research 102(D5):5885-5894

### CH<sub>4</sub> WMO Scale:

Dlugokencky, E. J., R. C. Myers, P. M. Lang, K. A. Masarie, A. M. Crotwell, K. W. Thoning, B. D. Hall, J. W. Elkins, and L. P. Steele (2005), Conversion of NOAA atmospheric dry air CH<sub>4</sub> mole fractions to a gravimetrically prepared standard scale, J. Geophys. Res., 110, D18306, doi:10.1029/2005JD006035.

CO WMO Scale:

Novelli et al., Development and evaluation of a gravimetric reference scale for measurements of atmospheric carbon monoxide, 1991, JGR, 96, 13109-13121, 1991.

N<sub>2</sub>O WMO Scale:

Hall et al., The NOAA nitrous oxide standard scale for atmospheric observations, JGR, 112, D09305, doi:10.1029/2006JD007954, 2007.

Isotopic composition:

Trolier, M., J.W.C. White, P.P. Tans, K.A. Masarie and P.A. Gemery, Monitoring the isotopic composition of atmospheric CO<sub>2</sub>: measurements from the NOAA Global Air Sampling Network, JGR 101, 25,897-25,916 (1996).





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