NCAR/Scripps Medusa Flask Sampler Flask Data for the Atmospheric Tomography Mission, Version 2.0

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1 Data Set Overview

This data set includes measurements of $\delta(O_2/N_2)$, $\delta(Ar/N_2)$, and CO_2 abundance, made by the Scripps Institution of Oceanography (SIO) O_2 Program on flasks collected by the NCAR/SIO Medusa Whole Air Sampler (Medusa) for NSF/NASA Atmospheric Tomography Mission (2016–2018) on the NASA DC-8.

Please keep Britton Stephens updated if you are using these data in your analyses, so that he may provide input on their interpretation and apprise you of any updates.

2 Instrument Description

Medusa is an automated flask sampler for aircraft use that collects pressure- and flow-controlled, cryogenically dried air samples in 1.5 L borosilicate glass flasks. The specific configuration and operating conditions of the instrument has varied between campaigns. For a complete description of the Medusa flask sampler, in both its former and current configurations, the reader is referred to Stephens et al. [2020].

In brief, pressure was controlled both upstream and downstream of the flasks and pumps. The upstream vacuum pump and pressure controller worked in a feedback loop to maintain a constant low pump inlet pressure, whose value was below the lowest expected atmospheric pressure, in order to allow constant inflow of sample air. After passing through the inlet pump, sample air was immediately cooled and dried in two electropolished stainless steel cryotraps immersed in a slurry of dry ice and Fluorinert with a temperature of approximately -78°C. The dried air was then directed to the inlet of one of the 32 flasks by a series of valves. A second pump and pressure controller downstream of the flask outlets controlled sample pressure to approximately one atmosphere. The flasks are equipped with two valves; the outlet valve is connected to a diptube to minimize fractionation effects during filling. During flight two upstream pressure controller settings were used: a low altitude setting and a high altitude setting. The operator typically sampled at the high altitude setting only when the aircraft was at altitudes greater than 32 kft, though this cutoff varied between campaigns. The flasks were sealed by Viton o-rings lightly greased with Apezion. Flasks were shipped to SIO for analysis; the mean sample storage time for all flasks was 81 days.

3 Data Collection and Processing

Sampled flasks were analyzed at SIO for $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ on a GV Instruments Micromass IsoPrime isotope ratio mass spectrometer (IRMS), and for CO_2 on a LI-COR LI-6252 nondispersive infrared (NDIR) analyzer. The IRMS analytical approach was first described by Bender et al. [1994], and further developed by Keeling et al. [2004]. During the analysis procedure, each flask was purged from the end of the flask forwards (in through the dip tube) with a "push" gas of known composition at a rate of 30 sccm for 5 minutes. Quantification is made by rapid switching between sample air and a reference gas of known composition.

Kernel files are included to facilitate comparison with real-time measurements, and provide a weighting function of the form:

$$w(t) = e^{-\left(\frac{t_f - t}{\tau}\right)} \tag{1}$$

where $w(t)$ is the weighting of any 1-second time increment t between the switch to the sample and the switch to the next sample, t_f, and τ is the flushing time in seconds, *i.e.*, the flask volume divided by the mean flow during the sampling period. The average flushing time for the high altitude setting was 38 seconds, and the average flushing time for the low altitude setting was 83 seconds. $w(t)$ is scaled so that it sums to 1 for all non-missing values over a given sampling interval.

3.1 Fractionation Correction

Observations of $\delta(Ar/N_2)$ made with Medusa often show significant vertical gradients deep into the troposphere, a trend suspected to be due to inlet fractionation [Bent, 2014]. Additionally, higher scatter of $\delta(Ar/N_2)$ in flasks sampled in the flask box closest to the floor indicated that thermal gradients were causing fractionation. We report $\delta(O_2/N_2)$ values that have been corrected for these two effects, assuming constant $\delta(Ar/N_2)$ in the troposphere but allowing for natural $\delta(Ar/N_2)$ gradients in the stratosphere. The atmospheric oxygen data is then corrected assuming a fixed Ar to O_2 relationship. A detailed description of this process, along with further rationale, is given in Stephens et al. [2020]. Briefly, stratospheric flasks are identified through their associated, kernel-weighted N_2O value, when available. All remaining flasks are considered to be tropospheric, and their $\delta(Ar/N_2)$ values are fit with a first-order loess curve (with a span of 0.2) as a function of atmospheric pressure. This trend is extrapolated with atmospheric pressure to estimate the inlet-fractionation effect for all stratospheric flasks.

All tropospheric $\delta(O_2/N_2)$ values are then adjusted by the difference between the observed $\delta(Ar/N_2)$ value and 15 per meg (an approximate tropospheric mean from the SIO network), scaled by 1/3.77. All stratospheric $\delta(Ar/N_2)$ values, adjusted for inlet fractionation, are regressed against N_2O, forced through an intercept of 15 per meg (such that a flask taken at the tropopause would have a $\delta(Ar/N_2)$ value of 15); the difference of the observed value from the expected value based on this regression is taken to be the magnitude of the scatter created by thermal fractionation. While the scatter removed by this correction incorporates natural $\delta(Ar/N_2)$ variations, it does retain the majority of the variability of $\delta(Ar/N_2)$ in the stratosphere, while reducing scatter believed to be caused by fractionation due to a combination of inlet-related effects, thermal fractionation within the flask, and any artifacts caused by storage. The resulting argon-corrected $\delta(O_2/N_2)$ values are referred to as $\delta(O_2/N_2)$* [Stephens et al., 2020].

4 Data Format

There are two files produced for each flight. The first, with a naming convention of "MEDUSA_DC8 _YYYYMMDD_Rx_.ict" contains flask concentrations and location information, with the following variables:

- Start_UTC: time of flask opening
- Stop_UTC: time of flask closure
- Mean_UTC: kernel-weighted representative sampling time
- position: flask position; an integer between 1 and 32, indicating the position in Medusa. Box1 is 1-16, Box2 is 17-32.

- upstream_pressure: kernel-weighted pressure reading at upstream pressure controller in torr
- downstream_pressure: kernel-weighted pressure reading at downstream pressure controller in torr
- bypass_pressure: kernel-weighted pressure of bypass line
- sample_pressure: Kernel-weighted average sample line pressure (i.e. at time of flask close) in torr.
- flow: Kernel-weighted calibrated flow rate through Medusa in mL/min.
- flask_pressure: fill pressure of each flask in torr
- O2N2_MED: $\delta(O_2/N_2)$ in units of per meg, on the SIO2017 O_2/N_2 scale, archive reference date 2020-10-09-17.11.44
- ArN2_MED: $\delta(Ar/N_2)$ in units of per meg, on the Scripps Ar/N_2 scale, archive reference date 2020-10-09-17.11.44
- O2N2star_MED: This is the same variable as d(O2/N2)*, discussed in this document and Stephens et al. [2020].
- CO2_MED: dry air mole fraction of CO_2 in units of ppm on the the Scripps O_2 Laboratory CO_2 Scale, archive reference date 2020-10-09-17.11.44
- d13CO2_MED: $\delta^{13}C$ of CO_2, in per mille (‰), relative to V.P.D.B.
- d18OCO2_MED: $\delta^{18}O$ of CO_2, in per mille (‰), relative to V.P.D.B.
- D14CO2_MED: $\Delta^{14}C$ of CO_2, in per mille (‰)

The second file, with a naming convention of "MEDUSA_YYYYMMDD_flight _kernel.txt", contains the weighting kernel, with the following variables without header names (from left to right):

- Start_UTC: Time, in seconds since 0000 UTC on day of takeoff.
- Kernel: The kernel weight of each timestep determined from Equation 1.

Spaces separate columns, and "NA"s represent missing values. The reported times have been adjusted for inlet delays and correspond to when the air entered the inlet.

5 Data Remarks

Data points corresponding to positions 1–16 generally display more scatter in $\delta(Ar/N_2)$ than data points corresponding to positions 17–32. This is believed to be due to larger thermal gradients, since positions 1–16 are located in a box that is closer to the floor of the aircraft, and thus nearer to the GV air conditioning vents [Bent, 2014].

The user should also be aware that the argon-corrected O_2 data should formally be considered a distinct quantity from that of the uncorrected oxygen data, since some of the correction applied actually incorporates the small natural variability of $\delta(Ar/N_2)$ expected in the troposphere.

References

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