Microdrop calibration of Picarro analyzer HIDS2380 for carrier gas N_2 and synthetic air and three laboratory standards FARLAB report 01-2020

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1 Introduction

The Picarro water vapour analyzers exhibit a dependency of the raw measurement of isotope ratios on humidity, that is different for different isotope ratios. Characterising the instrument across this two-dimensional parameters space is essential when using the analyzers in low-humidity environments with a substantial range of (previously unknown) isotope ratios.

We have previously characterised this parameter space using autosampler injections and the Picarro SDM (Weng et al., 2019). Neither of these methods is designed to provide a vapour stream at much lower humidity than the default range of about 10'000 to 25'000 ppmv. At FARLAB, we have built a new calibration device, based on earlier work by Iannone et al., 2009, based on a droplet ejector (Microdrop GmbH, Germany).

The present report summarizes the first application of the prototype of the FARLAB microdrop evaporator to test the isotope-ratio humidity dependency of the instrument HIDS2380. This instrument has previously been observed to have a much stronger dependency than other instruments we have at FARLAB. The issue has been examined by Picarro technicians, and they attempted a recalibration of the humidity dependency, as detailed below. However, no change could be observed after the modifications of the pressure calibration by Picarro engineers on 17 Jan 2020.

Using instructions from Picarro on how to calibrate the humidity dependency, we have changed the fitting parameters on 14-15 May 2020 in the instrument as detailed below. This results in a much more linear response of the instrument across a humidity range from 20'000 to 3200 ppmv.

We use the results from this calibration report to correct the previous measurement data obtained from this analyzer during side-by-side measurements at the GFI tower observatory, and since 15 May 2020 use a different correction, that will have to be determined using the microdrop calibration device.

2 Setup

The Microdrop calibrator has been connected to the inlet of the HIDS2380 with a t-piece, connected to the WLM with a check valve to prevent ambient air flowing into the analyzer.

The microdrop evaporator provided typically 110 sccm of dry carrier gas, heated to between 45-60°C. The single dispenser head dispensed lab standard from a vial, with a holding pressure between -10 to -12 hPa. Initially, the dispenser head was controlled manually via the Microdrop touch screen, and later by a custom python control script. The main parameter to change humidity was to step up the dispenser head frequency within a range of 10 to 250 Hz.

Calibration runs have been performed using either N_2 or synthetic air as a carrier gas. Runs were thereby either performed by stepping up from 10 Hz or down from 250 Hz initial frequency. An alternating pattern was used for quickly transitioning between two frequencies. For example, when stepping up from 10 to 20 Hz, a 30 Hz frequency was used for a brief initial period, then 15, then 25 and so on.

The transition period between two concentrations was removed before further analysis, ranging typically between 1.7 and 2.1 min. The duration of the stable runs was 5 min, later also 10 min.

Humidity ranged typically between about 1'000 and 26'000 ppmv (raw) in steps between 15 and 23. The precision was typically 20–30 ppmv (median of one-sigma standard deviation over a 5 min period for a full run), with a range of 10 to 300 ppmv.

The humidity sequence of a typical run is shown in Fig. 1. Not all runs performed similarly well, some broke down after a shorter number of steps, others had high variability for some of the steps, in particular for high humidity range, and for later runs.

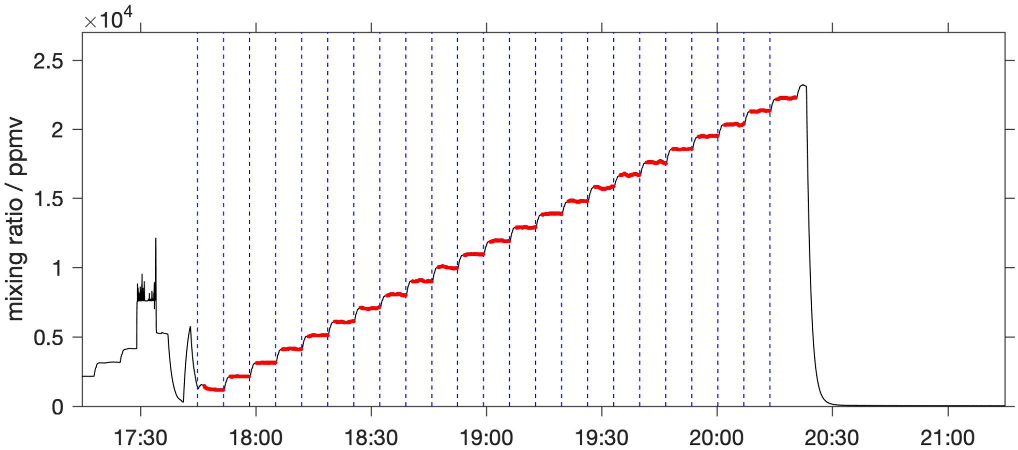

Figure 1: Typical humidity sequence during a calibration run on the FARLAB microdrop evaporator. Example depicts run 2 with carrier gas synthetic air, standard GSM1 on 25 Nov 2019, with 19 steps of 5 min duration.

For both carrier gases, three FARLAB laboratory standards were used, GSM1, VATS and EVAP. Their isotope ratios according to the latest calibration from 2017 are reported in Table 1.

Details of the setup for all 11 runs performed on the HIDS2380 are given in Table 2.

The matlab script for processing the raw measurement data is located in `FARLAB/Reports/Cal_HIDS2380/iso_hum_dep_HIDS2380.m`. The analysis is based on Picarro raw data files converted to netCDF format within regular FARLAB data management routines.

	Picarro L2140-*i* (HKDS2038), FARLAB		
	δ^{18}O [‰]	δD [‰]	*d*-excess [‰]
GSM1	-33.07 ± 0.02	-262.95 ± 0.04	1.63 ± 0.17
VATS	-16.47 ± 0.02	-127.88 ± 0.09	3.89 ± 0.18
EVAP	5.03 ± 0.02	4.75 ± 0.11	-35.47 ± 0.16

Table 1: δ values of lab standards, calibrated against IAEA standards on May 18, 2017. Uncertainty reported as 1-σ standard deviation of the mean. Isotopic dependency on water concentration is corrected (according to the second version of humidity dependency function).

Table 2: Sequence of all microdrop calibration experiments on the HIDS2380. Offset and duration in minutes. Fitting parameters are slope and offset of linear fits up to 5000 ppmv.

Gas	Standard	Start date	Steps	Offset	Duration	fit δ^{18}O		fit δD	
Air	GSM1	24-11-2019 17:44:50	23	1.77	5.00	-2.25e-03	22.4	-1.13e-03	11.4
Air	GSM1	25-11-2019 09:29:20	19	1.77	5.00	-2.25e-03	22.5	-1.09e-03	10.9
Air	GSM1	28-11-2019 10:02:50	19	1.88	5.00	-2.25e-03	22.5	-1.11e-03	11.1
Air	GSM1	23-01-2020 21:23:40	25	2.05	5.00	-2.31e-03	23.0	-1.38e-03	13.4
N_2	GSM1	22-11-2019 17:37:50	19	1.97	5.00	-2.41e-04	2.35	-9.89e-04	9.56
N_2	GSM1	01-12-2019 15:09:50	18	2.05	5.00	-2.90e-04	2.79	-1.03e-03	9.92
N_2	GSM1	24-01-2020 15:15:50	22	2.05	5.00	-2.31e-04	2.43	-1.06e-03	10.5
N_2	VATS	11-12-2019 20:24:50	21	2.05	5.00	-2.61e-04	2.63	-9.25e-04	9.18
N_2	VATS	12-12-2019 08:51:50	23	2.05	5.00	-2.25e-04	2.23	-8.78e-04	8.57
Air	VATS	13-12-2019 08:27:20	16	2.05	5.00	-2.21e-03	22.0	-9.42e-04	9.33
Air	VATS	15-12-2019 20:34:20	18	2.05	5.00	-2.25e-03	22.5	-9.23e-04	9.14
Air	EVAP	16-12-2019 10:12:50	21	2.05	5.00	-2.36e-03	23.5	-1.19e-03	11.8
N_2	EVAP	17-12-2019 10:24:20	17	2.05	10.00	-3.06e-04	2.72	-8.35e-04	6.90

3 Results

The results of the characterisation are reported on charts displaying δ^{18}O and δD vs. mixing ratio (Fig. 2 and Fig. 3). Several runs are shown on one panel when both upward and downward steps were performed to detect potential hysteresis effects. The one-sigma standard deviation for each 5-min averaging interval is displayed as vertical bars.

3.1 Synthetic air carrier gas

Using synthetic air as a carrier gas, the isotope-ratio humidity dependency is very strong with regard to mixing ratio for O-18 (Fig. 2, left column). This is unlike any other dependency measured on FARLAB analyzers, or seen in publications. According to Picarro technical service, this is not the intended behaviour, and the manufacturer is currently looking into this issue.

With regard to the isotope-ratio dependency, there is virtually no variation between the three standards. Thus, we can to first order correct the isotope-ratio humidity dependency with one constant function. The slope is -2.21 to -2.36 permil per 1000 ppmv, according to the linear fits above 5000 ppmv (Table 2). However, it is possible that the strong first-order dependency masks a more subtle second-order dependency.

No change is observed between the runs before (crosses) and after (circles) re-calibration by Picarro engineers on 17 Jan 2020.

For δD, there is also a strong dependency on mixing ratio (Fig. 2, right column). The slope is -0.92 to -1.19 permil per 1000 ppmv, according to the linear fits above 5000 ppmv (Table 2).

Interestingly, there is also a dependency on isotope ratio in the low-humidity range. Below about 5000 ppmv, the curvarture switches from upward for GSM1 (confirmed by upward and downward steps) to flat (VATS) and downward (EVAP). Correction of these measurements will be more intricate, but it remains to be seen if any of the data series from the GFI tower reached such low humidities.

Within the uncertainty bounds, there is no discernible hysteresis from stepping either upward or downward in mixing ratios.

No change is observed between the runs before (crosses) and after (circles) re-calibration by Picarro engineers on 17 Jan 2020.

3.2 N_2 carrier gas

Using N_2 as a carrier gas, we note a substantially smaller humidity dependency for each of the standards as in the previous experiments (Fig. 3). More specifically, the slope is -0.225 to -0.306 permil per 1000 ppmv for δ^{18}O, and -0.835 to -1.03 permil per 1000 ppmv for δD.

At the lower humidity ranges, the curves exhibit a maximum, reminiscent of earlier published dependencies (Weng et al., 2019). Interestingly, the isotope-ratio dependency almost non-existent for δ^{18}O (Fig. 3, left column).

For δD, the overall range and shape of the isotope-ratio humidity dependency is pronounced with humidity, stronger than for other FARLAB analyzers, but not as strong as with air carrier gas. Again, a maximum appears at about 5000 ppmv. There is some isotope-ratio dependency detectable for δD, as the bend gets stronger for less depleted standards.

The present results for N_2 as a carrier gas do not indicate the existence of hysteresis effects between upward and downward runs.

4 Mixing ratio dependency recalibration

Picarro engineers logged on remotely to adjust the pressure dependency calibration parameters of the instrument. After additional tests with the humidity dependency was again checked after 17 Jan 2020, and turned out to be unchanged.

On 14-15 May 2020, we followed the instructions from Picarro to recalibrate the water vapour concentration dependency. In the file `C:\Picarro\G2000\InstrConfig\Calibration\InstrCal\fitterconfig.ini`, there are parameters for linear and quadratic fits, for either N_2 or air carrier, named AIR_offset1, AIR_offset3, AIR_G1_quadratic, etc. These were reset to factory settings, and then the offsets stepwise modified at different concentrations (20'000 ppmv and 3200 ppmv). Due to the linear response to these offsets, the intersection of the two lines, provided the setting with the most constant humidity response for a given AIR_offset1 and AIR_offset3. The detailed routines are explained in the document "Picarro H2O concentration dependence - customer instructions.docx", attached as PDF to this file (Fig. 4), and isotope values for one standard (DI) are found in Table 3, with corresponding charts in Fig. 5.

The analysis needs to be repeated for N_2, and a isotope-composition humidity dependency needs to be established using a sequence of runs on the microdrop calibration device.

5 Conclusions

1. Based on the analysis performed here, we will be able to correct previous measurements of ambient air with the HIDS2380 within the humidity range of up to 5000 ppmv with a linear relation. Correction of measurements with lower humidity will be more intricate.
2. Before further measurements in the low mixing ratio range, the instrument now needs to be finally calibrated across a range of lab standards, and for pressure and absolute humidity.
3. Fitting parameters need to be deterimined and checked for N_2 as well.

References

- Weng, Y., A. Touzeau and H. Sodemann, 2019: Impact of isotope composition on the humidity dependency correction of water vapour isotope measurements with infra-red cavity ring-down spectrometers, Atmos. Meas. Techn., doi:10.5194/amt-2019-316, in revision.
- Weng, Y., Report on FARLAB lab standards calibration (201705), FARLAB report 01-2017, 5 pp.
- Iannone, R.Q, D. Romanini, S. Kassi, H. A. J. Meijer, and E. R. Th. Kerstel, 2009: A Microdrop generator for the calibration of a water vapor isotope ratio spectrometer, J. Atm. Ocean. Techn., Vol. 26 (6): 1275–1288, doi:10.1175/2008JTECHA1218.1.
- Sodemann, H., Specification calculations for a Microdrop humidity generator, FARLAB report 01-2018 (updated 19.07.2019), 5 pp.

Table 3: Determining parameters AIR_offset1 (O-18) and AIR_offset3 (H-2) from repeated SDM calibrations with standard DI. Final values shown in bold face.

AIR_offset1	2600 ppmv	3200 ppmv	20000 ppmv	AIR_offset3	2600 ppmv	3200 ppmv	20000 ppmv
-0.46	-	-11.9	-14.1	0.13	-	-61.9	-43.77
-0.44	-	-12.0	-14.1	0.53	-	-54.77	-42.35
-0.4	-	-12.0	-	1.40	-	-38.95	-40.33
-0.2	-	-11.5	-	**1.32**	-43.6	-	-41.4
-0.86	-	-12.55	-14.15	1.6	-	-	-
-2.06	-	-14.7	-	-	-	-	-
-1.73	-	-14.22	-14.36	-	-	-	-
-1.85	-15.67	-14.39	-14.47	-	-	-	-

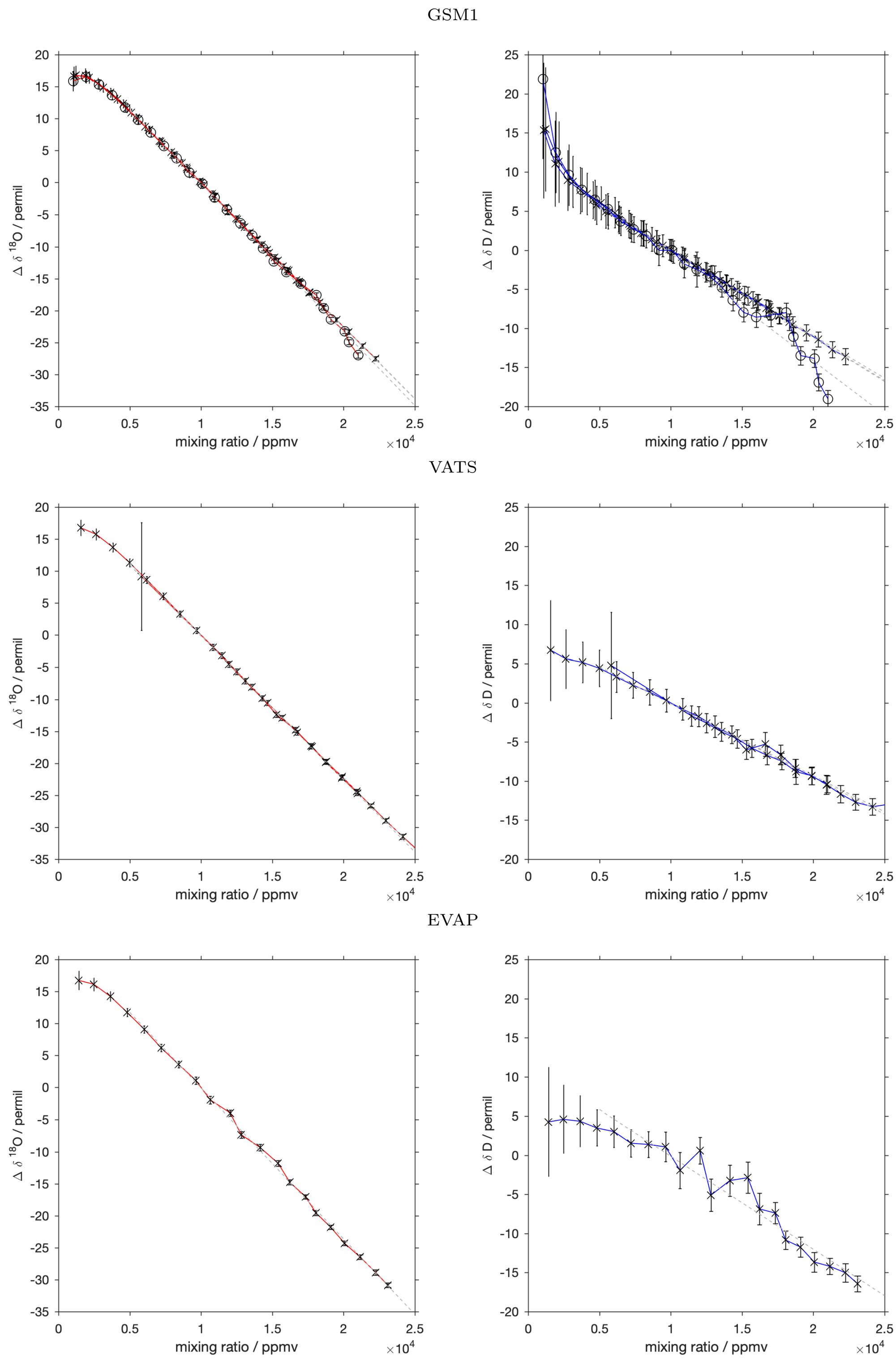

Figure 2: Isotope ratio-humidity dependency obtained from the microdrop evaporator for the three laboratory standards GSM1 (top), VATS (center) and EVAP (bottom) using synthetic air as as carrier gas. Crosses indicate runs before re-calibration by Picarro 17 Jan 2020, circles for runs thereafter.

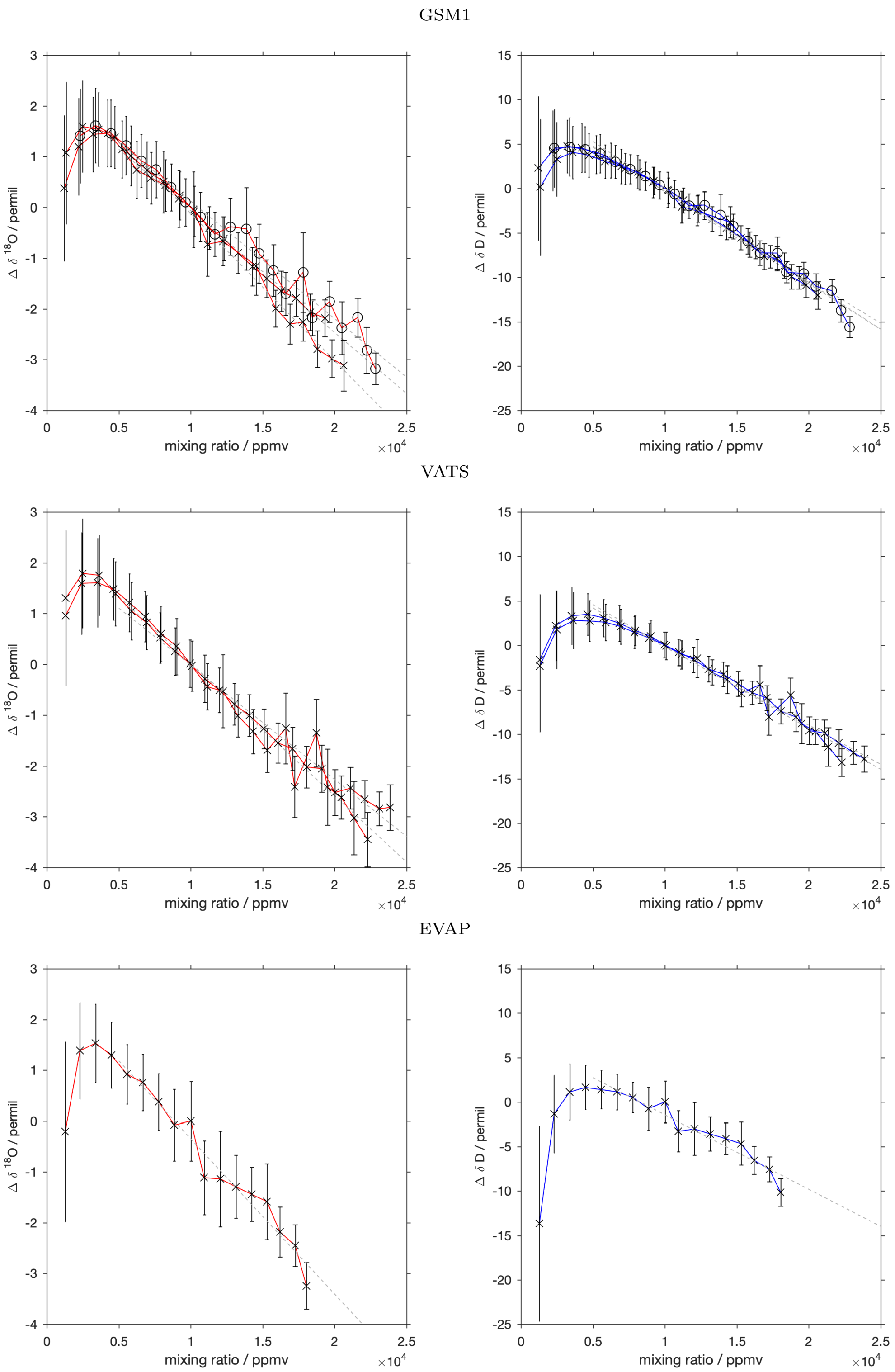

Figure 3: Isotope ratio-humidity dependency obtained from the microdrop evaporator for the three laboratory standards GSM1 (top), VATS (center) and EVAP (bottom) using N_2 as as carrier gas. Crosses indicate runs before re-calibration by Picarro 17 Jan 2020, circles for runs thereafter.

Instructions for adjusting:

1. Select 2 test points: 1 high, 1 low. From your experimental results, I recommend 1250ppmv and 25000ppmv.
2. Use these test results to determine the adequacy of the fit.
3. There are 2 fit parameters for each 18O and D and each carrier gas: Offset and quadratic. You will find these in the file C:\ Picarro\G2000\InstrConfig\Calibration\InstrCal\fitterconfig.ini.

```
Autodetect_enable = 0
N2_flag = 0

# Fitter configuration parameters from step test performed

AIR_offset1 = -0.46
AIR_offset2 = 0.0
AIR_offset3 = 0.13
AIR_G1_quadratic = -2.95E-05
AIR_G2_quadratic = 0.0
AIR_G3_quadratic = -2.45E-06
N2_offset1 = 0.09
N2_offset2 = 0.0
N2_offset3 = -0.15
N2_G1_quadratic = -2.75E-06
N2_G2_quadratic = 0.0
N2_G3_quadratic = -2.55E-06
```

4. Offset1 and quadratic1 are for 18O. Offset3 and quadratic3 are for D.
5. There is a method to fit and calculate these parameters, but it is complicated and iterative in any case, so our recommendation is to start with our test results and iterate from there with small changes. When we do the testing here, we do our standard broad range H2O correct and then perform low flow flatten for the flight analyzer. The low flow flattening changed the quadratic term significantly. Given that, and your poor test results, the first iteration recommended is to change the quadratic terms to the broad range results, which are:

a2, quadratic	N2_peak1_quadratic	O18 N2	-1E-06
a2, quadratic	N2_peak3_quadratic	D N2	-8.1E-07
a2, quadratic	Air_peak1_quadratic	O18 ZA	-1.1E-06
a2, quadratic	Air_peak3_quadratic	D ZA	-9.7E-07

We also recommend performing the adjustments on a single carrier gas to completion before starting the other carrier gas.

6. If the above quadratics improve the results, continue to use them without changes going forward.
7. Adjust the offsets by 0.01 increments are decrements. Repeat the 2 concentration test. The offsets are linear so improvement in results indicates that you should continue changing the offsets in the same direction.
8. Once the 2 concentration test shows satisfactory results, perform a multiple concentration verification test.

Figure 4: Picarro H_2O concentration dependency adjustment procedures.

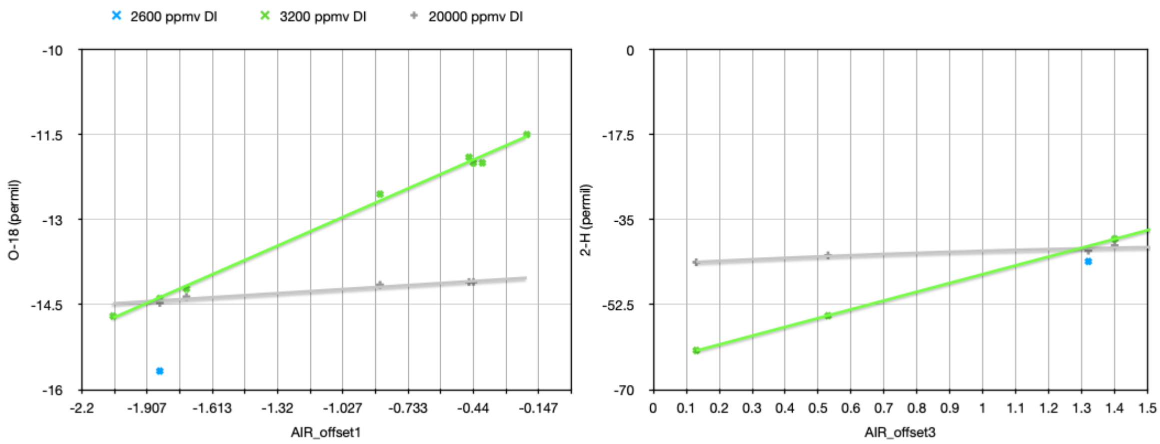

Figure 5: Linear dependency of isotope ratio on mixing ratio for standard DI using different values of fitting parameter AIR_offset1 (O-18) and AIR_offset3 (H-2). Source file: HIDS2380_fitter_cal.numbers