

Microdrop calibration of Picarro analyzer HIDS2380 for carrier gas N₂ and synthetic air and three laboratory standards

FARLAB report 01-2019

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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, an issue that is currently examined by Picarro technicians. Meanwhile, 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.

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 N₂ 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.

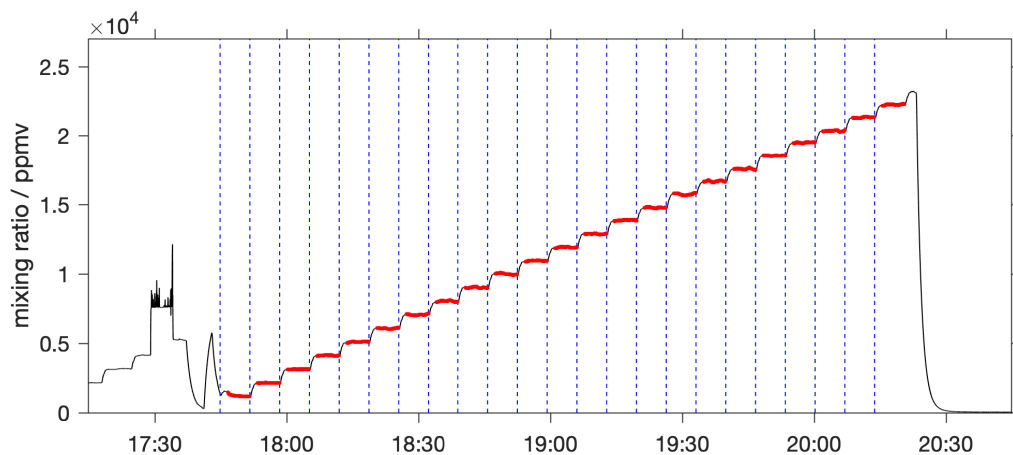


Figure 1: Typical humidity sequence during a calibration run on the FARLAB microdrop evaporator. Example depicts run 2 with carrier gas synthetic air, standard GSM1 on 25 Nov 2019, with 19 steps of 5 min duration.

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.

	Picarro L2140- <i>i</i> (HKDS2038), FARLAB		
	$\delta^{18}\text{O}$ [‰]	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).

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.

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 $\delta^{18}\text{O}$	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
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	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 $\delta^{18}\text{O}$ 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.

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 curvature 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.

3.2 N₂ carrier gas

Using N₂ 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 $\delta^{18}\text{O}$, 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 $\delta^{18}\text{O}$ (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 N₂ as a carrier gas do not indicate the existence of hysteresis effects between upward and downward runs.

4 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. The analyzer is currently under investigation by Picarro to remove or adjust the documented behaviour. If remote tuning is not successful, the analyzer may have to be returned to Picarro for service.
3. It is not recommended to make further measurements with the analyzer in its present state, in particular within the low humidity range. The uncertainty introduced from the correction is substantially larger than for comparable analyzers at FARLAB, and in the published literature.

References

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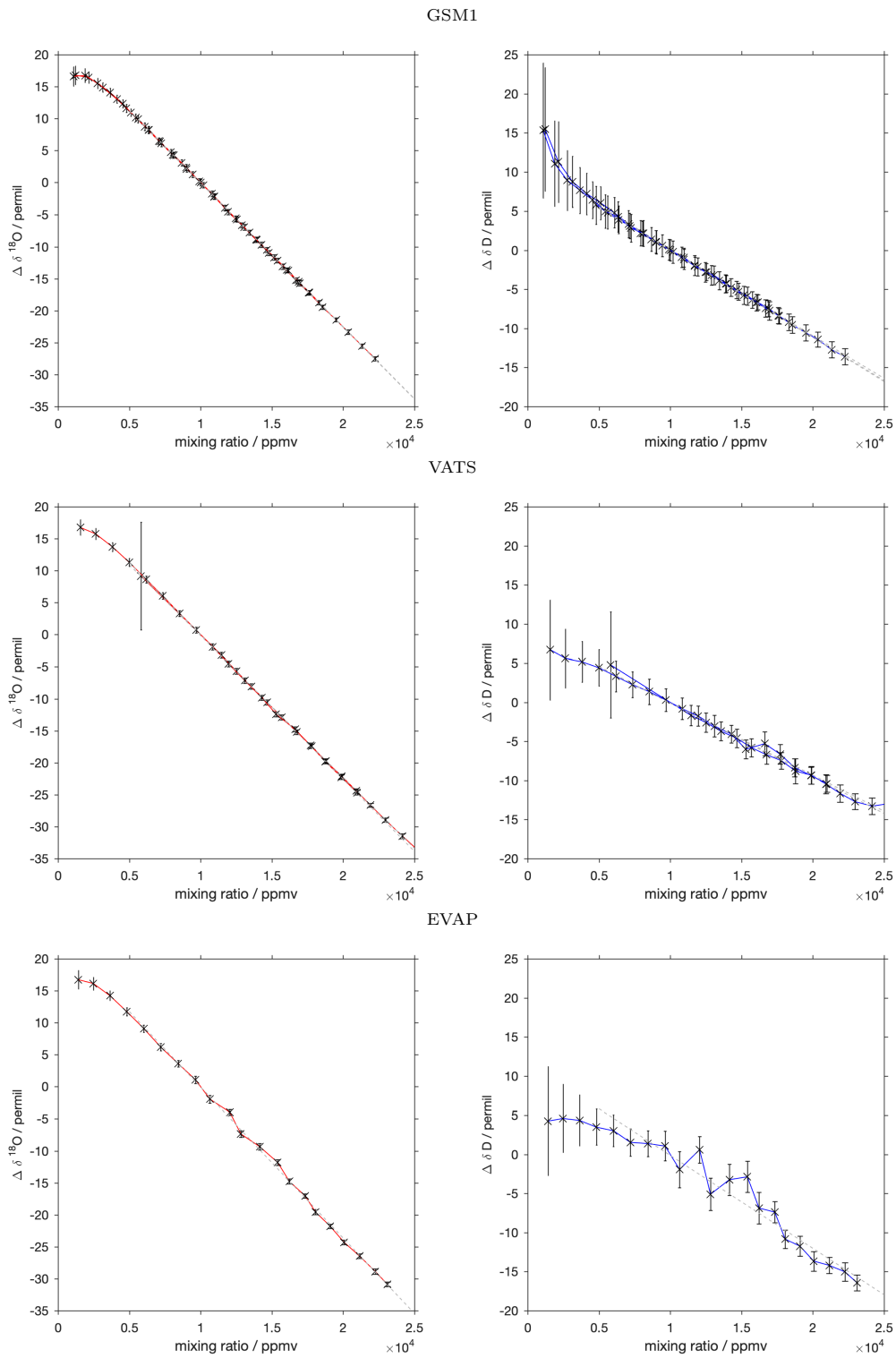


Figure 2: Isotope ratio-humidity dependency obtained from the microdrop evaporator for the three laboratory standards GSM1 (top), VATS (center) and EVAP (bottom) using synthetic air as carrier gas.

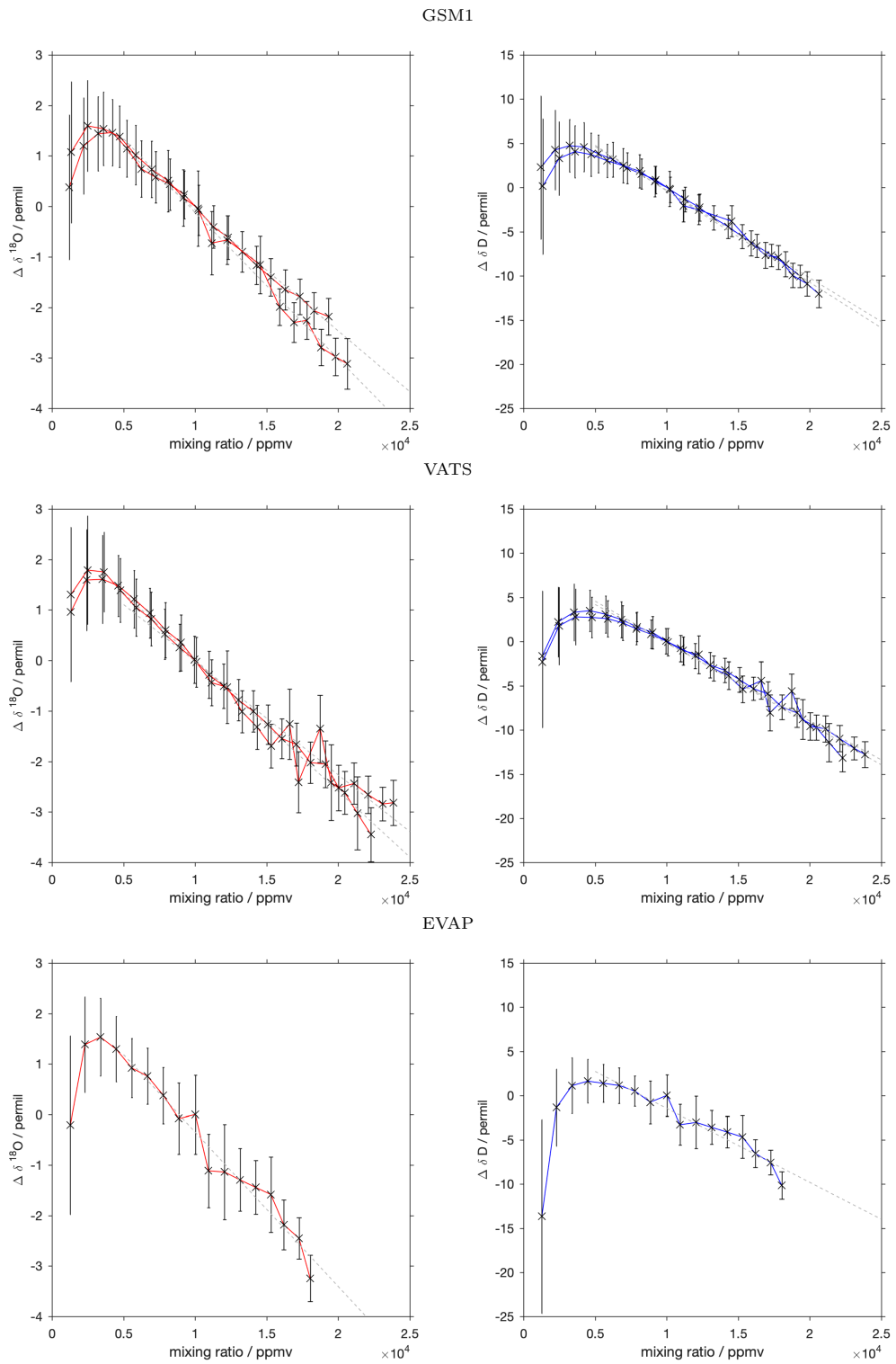


Figure 3: Isotope ratio-humidity dependency obtained from the microdrop evaporator for the three laboratory standards GSM1 (top), VATS (center) and EVAP (bottom) using N_2 as carrier gas.