

# Instrument Calibration of Picarro L2130-*i* (HIDS2254)

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## 1 Introduction

An important prerequisite for the interpretation of data is a detailed knowledge about instrument properties. Here is a basic characterisation regarding to the liquid injection measurement of a commercial laser spectroscopic system based on cavity ring-down spectroscopy (CRDS). Specifically, the calibrations presented here are only based on Picarro L2130-*i* (Module No.: HIDS2254) at FARLAB, University of Bergen (UiB).

The spectroscopic measurements of water isotopes are affected by the water vapour mixing ratio in two ways. (i) The precision of the measurement depends on the water vapour mixing ratio. For the commercial laser spectrometer of Picarro, the best performance is obtained within an optimal water concentration range of 19,000~21,000 ppmv (manual from Picarro, Inc.). As the water concentration deviates from this range, especially towards the low levels, the measurement uncertainty grows rapidly. (ii) The isotopic value of the measurement is biased by water vapour mixing ratio. This is often referred as *water concentration dependency*, i.e., the isotope ratio measured will change as a function of the water vapour mixing ratio. Water concentration dependency is most significant and a prominent source of measurement bias outside the instrument's optimal water concentration range. In the case of liquid injection measurement, for majority of the time the water concentration is maintained within the optimal range, so that the precision stayed stable at the best level and the water concentration dependency is kept minimum.

Water concentration measured by Picarro is normally not the true value. And the accuracy of the water concentration measurement can be estimated with a dew point generator. This process is referred as *absolute water concentration calibration*. The calibration can be useful when one wants to know the actual water vapour mixing ratio of the ambient air that has been measured by Picarro.

These calibration features/functions are based on the specific instrument at FARLAB, UiB and were assessed in laboratory experiments. They might be subject to change either after a certain period or due to relocation of the instrument (?). In this case, an independent instrument characterization will be required.

For the measurement of liquid samples, the water concentration is maintained normally within 19,000~21,000 ppmv (uncalibrated), in very few occasions within 16,000~24,000 ppmv. In this report, only the calibration regarding to the liquid injections is presented.

## 2 Water Concentration Dependency

The isotopic compositions ( $\delta$  values) measured by CRDS have a dependency on the water concentration. To determine the dependency function, we can measure a stable vapour source of fixed isotopic composition with changing water mixing ratio. There are typically three approaches to generate a stable vapour source: bubbling device such as a Dew Point Generator (DPG), continuous liquid delivery of liquid stream into a vaporizer by device such as Standard Delivery Module (SDM), and discrete liquid injections into vaporizer manually or by device such as Autosampler. Here we present calibration from liquid injections of 5 water standards, for an water concentration range of 15000-24000 ppm.

## 2.1 Calibration with a liquid autosampler

Figure 1 shows the averaged per mil deviations ( $\Delta\delta^{18}\text{O}$  and  $\Delta\delta\text{D}$ ) from the measured isotope values at 20 000 ppmv of five standards as a function of water vapour mixing ratio. The results have been fitted with a simple linear regression function. The fitting results are shown in below (number in brackets indicates standard deviation  $1\sigma$ ) and also in the legends of Figure 1.

$$\Delta\delta^{18}\text{O}: y = -2.3413 \times 10^{-5} (\pm 5.4750 \times 10^{-7})x + 0.46827 (\pm 0.0104)$$

$$\Delta\delta\text{D}: y = 3.4243 \times 10^{-5} (\pm 5.2200 \times 10^{-6})x - 0.68486 (\pm 0.0992)$$

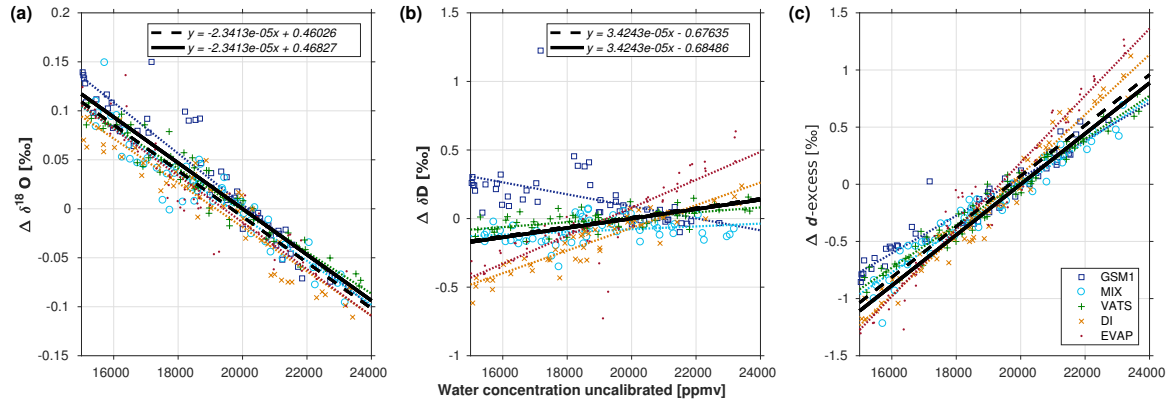


Figure 1: Isotopic dependency on water concentration in the range of 15000-24000 ppm for (a)  $\delta^{18}\text{O}$ , (b)  $\delta\text{D}$  and (c)  $d$ -excess. Five water standards of different isotope ratios from depleted to enriched are measured. Water concentration presented here are not calibrated. A linear fit is presented for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . Dotted lines are linear fits for each water standard; dashed line is a linear fit for all of 5 water standards; black thick line is the final fit by constricting the dashed line to cross the fixed point at [20000,0]. The fit for  $d$ -excess is calculated based on the linear fits of  $\delta^{18}\text{O}$  and  $\delta\text{D}$ .

## 2.2 Discussion on concentration dependence

A few factors could affect the determination of concentration-isotope response.

1. The remaining water vapour in the supplied dry air can affect the accuracy of the isotope ratio measured at very low water concentrations. In the case of the ambient air dried through Drierate, the residual humidity is much higher ( $\approx 300$  ppmv at the starting stage, but actually reaches to below 50 ppmv after a certain time, e.g., hours). In this case the background humidity might have an influence to the isotope ratio of the measured sample significantly at low humidity levels. This could result in a higher variability of the measurements especially at low humidities. In principle, the effect of remaining ambient water vapour in the carrier gas can be corrected. However, for such a correction a good estimate of the true isotope ratio of the carrier gas is needed, which is difficult to obtain due to the high uncertainty of isotopic measurements at very low humidity levels (Aemisegger *et al*, 2012). Even though using dried ambient air as a carrier gas implies the problem of residual ambient humidity, Aemisegger *et al* (2012) still preferred this approach for calibration in the field rather than air from a gas cylinder, with the consideration that its composition in terms of other trace gases is the same as for the sample gas measured.

2. In the case of dry synthetic air, after hours of flushing the measured background water concentration on Picarro is around 10 ppmv. In this case, the potential influence from the remaining air in the dry gas supply can be negligible (should be applicable to the case with dry air through Drierate as well). Thus the measurement is mainly affected by memory effects from the remaining vapour from previous measurements in the system, most likely in the vaporizer (if used), filter before cavity, cavity (small volume), and on the inner walls of the tubes.

3. The effect of methane cannot be excluded and is known to be an important interfering species especially at low humidity levels (Hendry *et al*, 2011).

### 3 Absolute Water Concentration Calibration

Water concentration measured by Picarro L2130-i was calibrated against dew point generator (DPG) on 2016-06-03 at FARLAB, UiB. The model used is LI-610, LI-COR Inc., Lincoln, NE, USA). The results have been fitted with a simple linear regression function and a quadratic function with an extra constraint point (0 ppmv, 0 ppmv). The fitting results are shown in below (number in brackets indicates standard deviation  $1\sigma$ ) and also in the legends of Figure 2 and Figure 3.

$$\text{Linear: } y = 1.0678(\pm 0.003)x - 511.9837(\pm 40.425)$$

$$\text{Quadratic: } y = 3.3331 \times 10^{-6}(\pm 1.7800 \times 10^{-7})x^2 - 0.9788(\pm 0.0029)x$$

For liquid injections whose water concentrations are typically in between 15000 and 24000 ppmv, a calibration with either of the fitting functions should not make a distinct difference. However, the quadratic function, as it passes the point of (0 ppmv, 0 ppmv), is currently recommended before the detailed calibration at low water concentrations (<6000 ppmv) is available.

1. Picarro mode: iH2O Flux Air & iH2O Air Low Flow; inlet flow rate  $\sim 72$  &  $\sim 32$  sccm, respectively.
2. Ambient air through dew point generator (LI-610); flow rate  $\sim 160$  &  $\sim 100$  sccm, respectively.
3. Ambient pressure is measured by Pfeiffer Vacuum (Gauge APR250), which has been calibrated against VAISALA barometer (see Appendix A).

Table 1: Experiment setup during absolute water concentration calibration.

Picarro mode	inlet flow rate	DPG* flow rate	dew point sequence [°C]
Flux Air	$\sim 72$ sccm	$\sim 160$ sccm	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 5, 1
Air Low Flow	$\sim 32$ sccm	$\sim 100$ sccm	1, 4, 8, 12, 16, 18, 1

\* Dew point generator (LI-610, LI-COR Inc., USA)

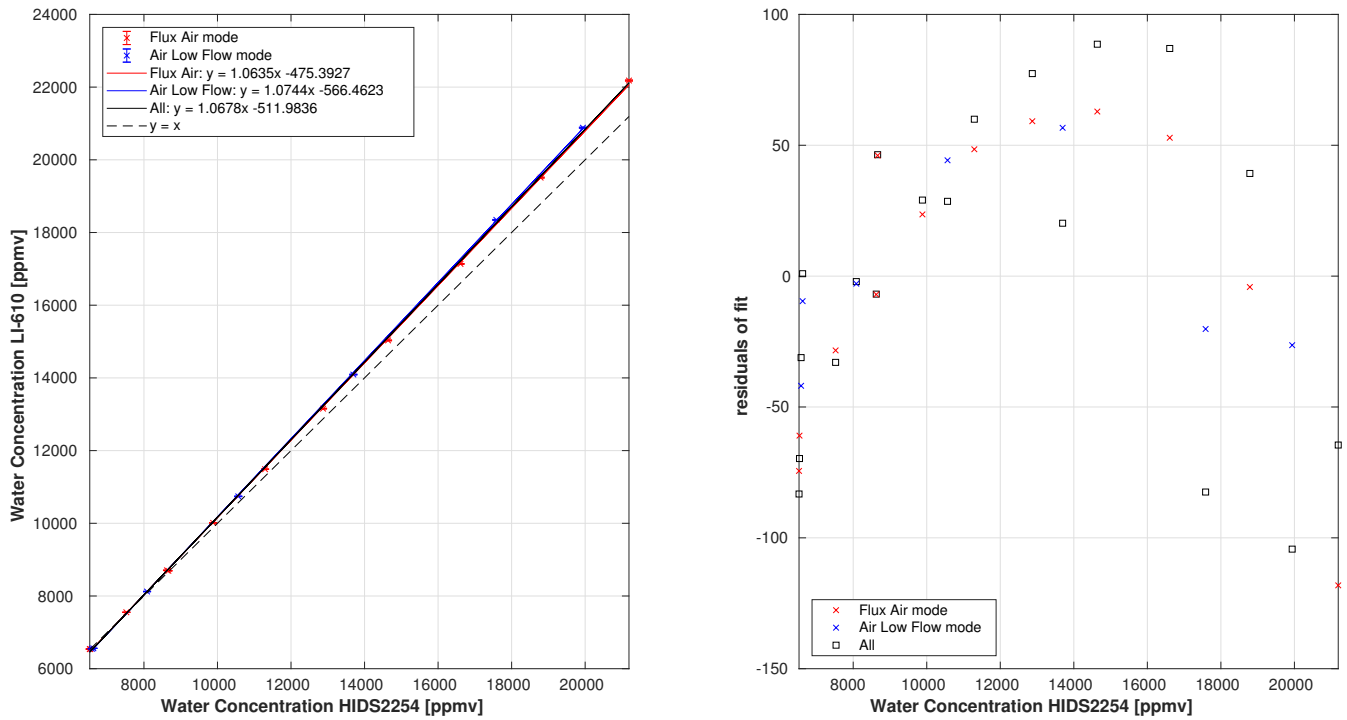


Figure 2: Water concentrations measured on Picarro CRDS (L2130) compared with the measurement on a dew point generator (LI-610). Dew points are in sequence set to 1°C, 3°C, 5°C, 7°C, 9°C, 11°C, 13°C, 15°C, 17°C, 19°C, 5°C, 1°C for iH2O Flux Air mode, and 1°C, 4°C, 8°C, 12°C, 16°C, 18°C, 1°C for iH2O Air Low Flow mode. Fitting is a linear regression function and the results are shown with solid lines.

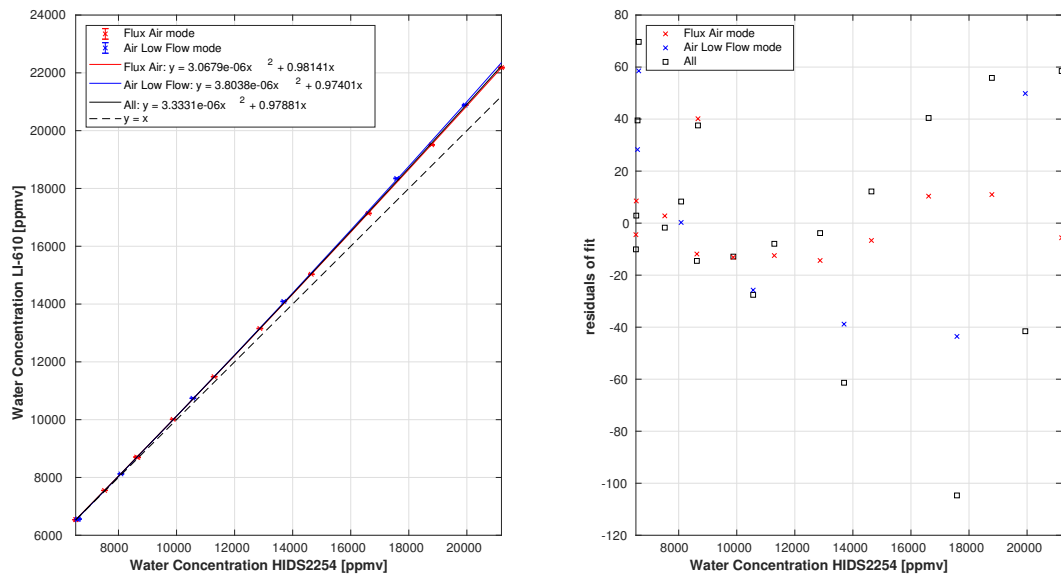


Figure 3: Water concentrations measured on Picarro CRDS (L2130) compared with the measurement on a dew point generator (LI-610). Dew points are in sequence set to 1°C, 3°C, 5°C, 7°C, 9°C, 11°C, 13°C, 15°C, 17°C, 19°C, 5°C, 1°C for iH2O Flux Air mode, and 1°C, 4°C, 8°C, 12°C, 16°C, 18°C, 1°C for iH2O Air Low Flow mode. Fitting is a quadratic function with an extra constraint point of (0,0) and the results are shown with solid lines.

## A Calibration of vacuum gauge (APR250)

The vacuum gauge (APR250, Pfeiffer Vacuum GmbH, Germany) with a single-channel measurement and control unit (TPG 261, SingleGauge<sup>TM</sup> INFICON AG, Pfeiffer Vacuum GmbH, Germany) has been calibrated against a digital barometer (PTB220TS, Vaisala Oyj, Helsinki, Finland). The two devices have been located close to each other to measure simultaneously the ambient pressure for 6 days. Results show that the pressure measured by vacuum gauge is about  $0.31 \pm 0.08$  hPa higher than that measured by the digital barometer. This discrepancy is overall constant over the range of measured ambient pressure (Figure 4 (left)). The calibration function can be well represented with a simple linear fit:  $y = x - 0.31$  (Figure 4 (right)).

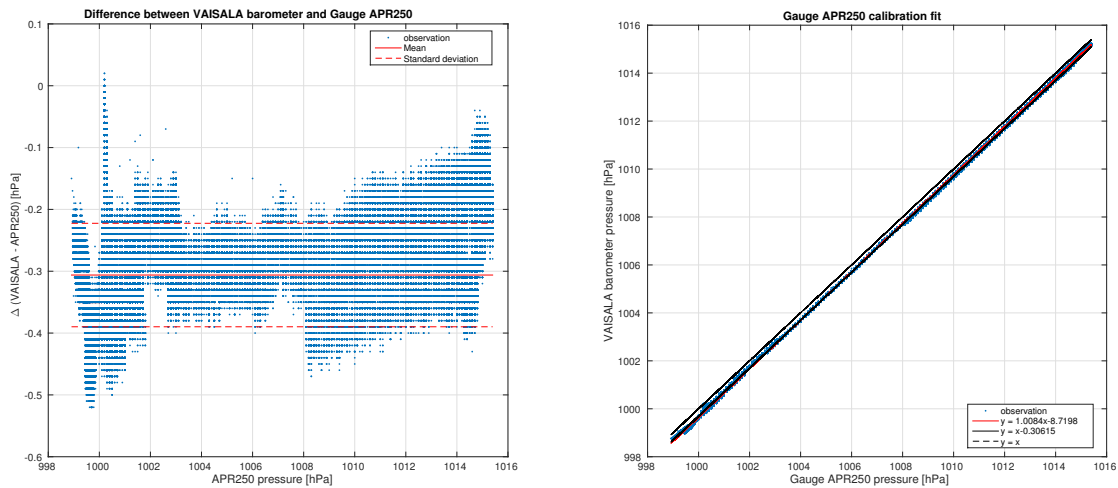


Figure 4: The discrepancy between the digital barometer (Vaisala) and the vacuum gauge (APR250) (left). The discrepancy is systematic and can be well represented with a simple linear fit:  $y = x - 0.31$  (right).