

# Instrument Calibration of Picarro L2140-*i* (HKDS2039) (Version 2)

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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 L2140-*i* (Module No.: HKDS2039) 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. 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.

## 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. Two approaches have been used for this calibration.

Picarro L2140-*i* (HKDS2039) is currently only used to measure liquid samples in vials. 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.

### 2.1 Calibration with a dew point generator

The first approach involves a dew point generator (DPG). During the calibration experiment, saturated water vapour at a certain dew point is generated from DPG. The water vapour is further mixed with

N<sub>2</sub> from gas cylinder to produce the required vapour source. The dew point is set to be 18°C as the ambient temperature is maintained to be around 20°C<sup>1</sup>. A range of water mixing ratios is reached by adjusting the flow rate of N<sub>2</sub>. The saturated water vapour at 18°C without N<sub>2</sub> mixing was measured at the beginning and end of the experiment to check the drift of the isotopic composition due to the evaporation that occurred while the unsaturated ambient air bubbled through the water reservoir inside the DPG.

To calculate the water concentration (in *ppmv*) of a saturated water vapour, the knowledge of both actual temperature and ambient pressure during the process is required. The temperature is obtained as the dew point set with DPG, while the ambient pressure is measured with a 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), which are available at FARLAB. The vacuum gauge has been calibrated against a digital barometer (PTB220TS, Vaisala Oyj, Helsinki, Finland). Details of the calibration for the vacuum gauge can be found in Appendix A.

Results of calibration with a DPG are shown in Figure 2. A linear fit in this section presents well the isotopic response.

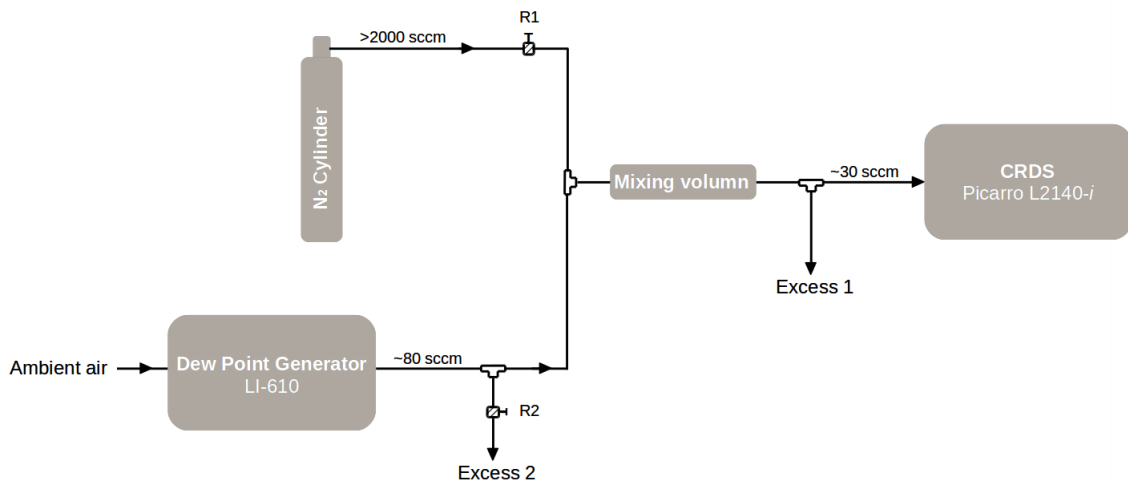


Figure 1: Flow diagram of the humidity calibration experiment with a dew point generator (DPG). During the experiment, the flow rate of DPG is set to be ~80 sccm. The N<sub>2</sub> cylinder provides an input over 2000 sccm at a constant pressure of ~1.7 bar. The flow rate of N<sub>2</sub> is further regulated with a regulator (R1) before mixing with the saturated water vapour. Regulator R2 remains closed, except in the case of generating a vapour source of extreme low water mixing ratio (<600 ppm). The CRDS is able to take ~30 sccm of the mixed water vapour, while the rest of it exits to the ambient at an excess outlet (Excess 1).

<sup>1</sup>The choice of 18°C is made such that the water concentration of the saturated water vapour can reach above 23,000 ppm and at the same time no condensation from the ambient air would occur in the water reservoir inside the DPG.

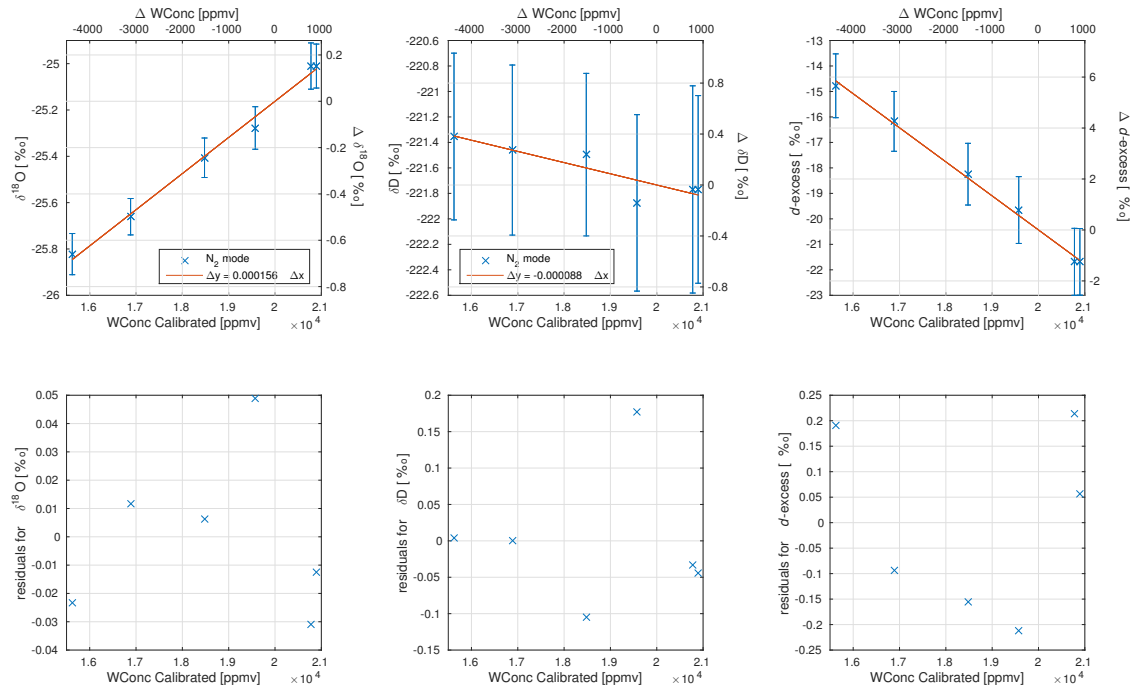


Figure 2: Isotopic dependency on water concentration in the range of 15000-21000 ppm. A linear fit is presented for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . The fit for  $d$ -excess is calculated based on the linear fits of  $\delta^{18}\text{O}$  and  $\delta\text{D}$ .

## 2.2 Calibration with a liquid autosampler

The average per mil deviations ( $\hat{\delta}^{18}\text{O}$  and  $\hat{\delta}\text{D}$ ) expressed with respect to the uncalibrated isotope values of the five standards at 20 000 ppmv are shown in Fig. 6 as a function of water vapour mixing ratio.

The effect of methane cannot be excluded and is known to be an important interfering species especially at low water vapour mixing ratios (Hendry et al., 2011).

In the case of the dried ambient air, the residual humidity is much higher ( $\hat{\delta}^{18}\text{O}$  100 ppmv) than in the dry synthetic air ( $\hat{\delta}^{18}\text{O}$  30 ppmv). The latter is only affected by memory effects from the walls of the tubing and the cavity. In the dried ambient air, however, the background water vapour mixing ratio influences the isotopic composition of the measured sample significantly at low water vapour mixing ratios. This results in a higher variability of the measurements especially at low water vapour mixing ratios. 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 isotopic composition of the carrier gas is needed, which is difficult to obtain due to the high uncertainty of isotopic measurements at very low water vapour mixing ratios.

Even though using dried ambient air as a carrier gas implies the problem of residual ambient humidity, we use it for calibration in the field rather than air from a gas cylinder, because its composition in terms of other trace gases is the same as for the sample gas measured.

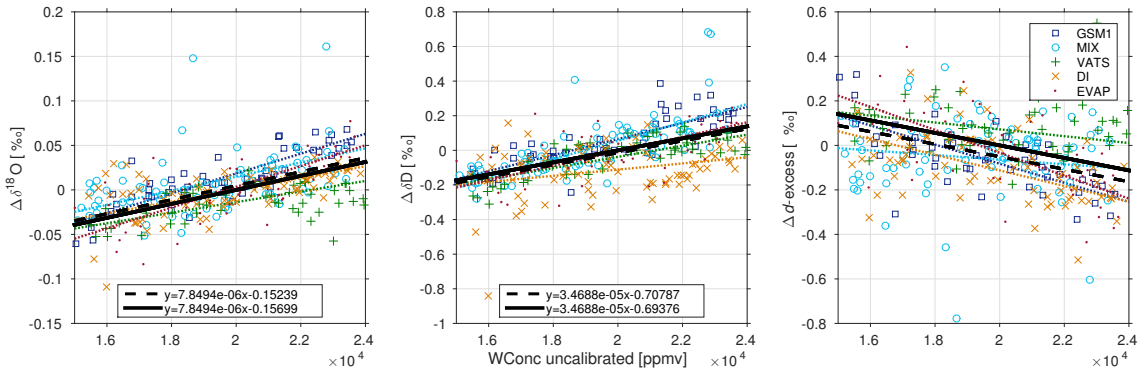


Figure 3: Isotopic dependency on water concentration in the range of 15000-24000 ppm. Five water standards are measured. Water concentration presented here are not calibrated. A linear fit is presented for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . Dotted lines are linear fits for each water standard; 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  $\delta\text{D}$ .

### 3 Absolute Water Concentration Calibration

Water concentration measured by Picarro L2140-i was calibrated against dew point generator (LI-610, LI-COR Inc., Lincoln, NE, USA) on 2016-06-06 at FARLAB, UiB.

1. Picarro mode: iH<sub>2</sub>O Air & iH<sub>2</sub>O N<sub>2</sub>; inlet flow rate  $\sim 32$  sccm.
2. Ambient air through dew point generator (LI-610); flow rate  $\sim 70 - 80$  sccm.
3. Ambient pressure measured by Pfeiffer Vacuum (Gauge APR250), which has been calibrated against VAISALA barometer.

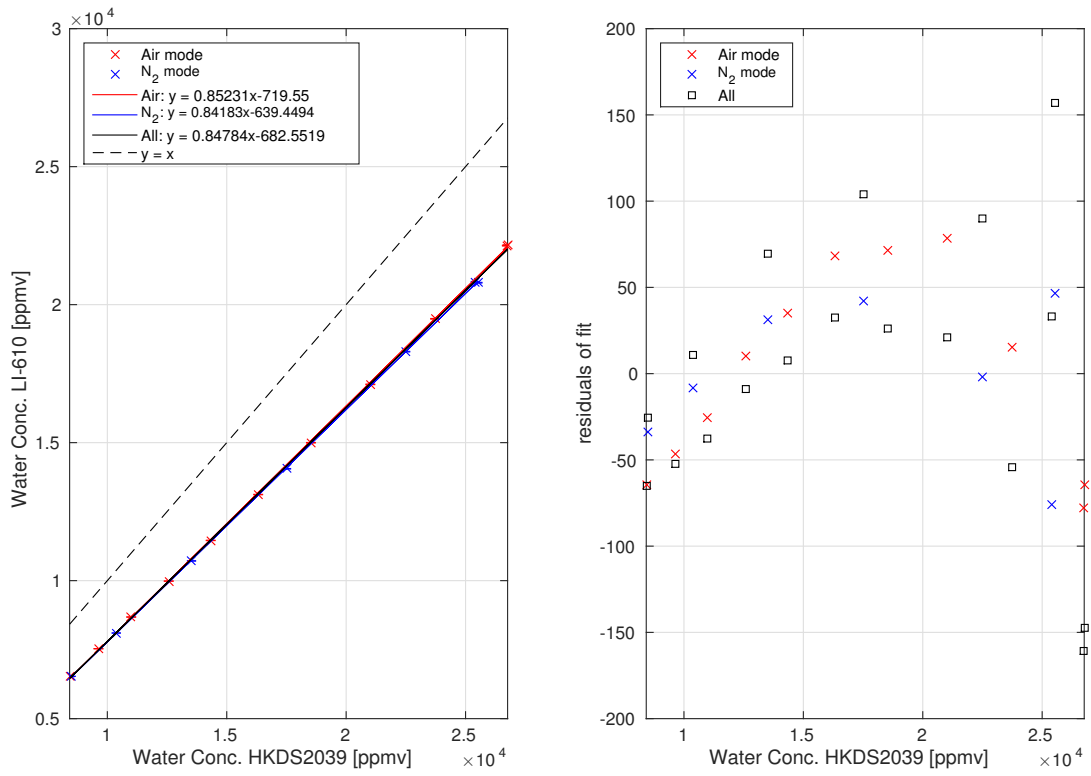


Figure 4: Water concentration calibration vs. dew point generator LI-610. Dew points are in sequence set to 19°C, 1°C, 3°C, 5°C, 7°C, 9°C, 11°C, 13°C, 15°C, 17°C, 19°C for air mode and 18°C, 1°C, 4°C, 8°C, 12°C, 16°C, 18°C for N<sub>2</sub> mode.

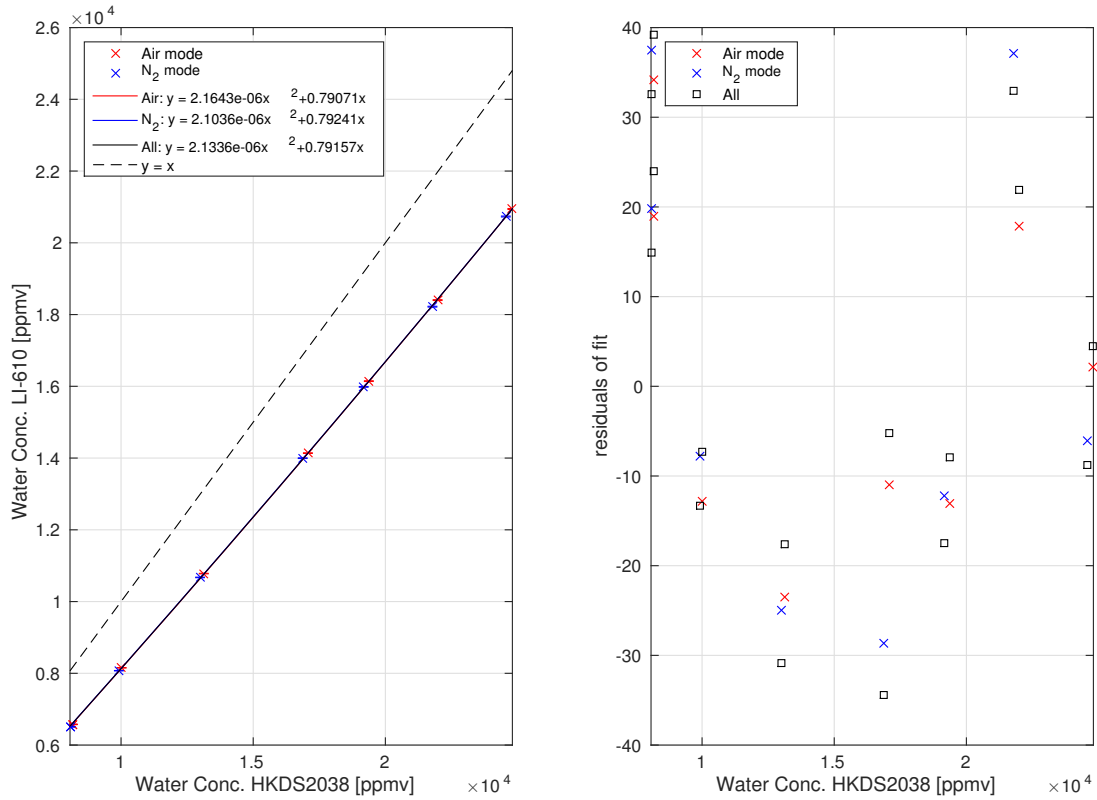


Figure 5: Water concentration calibration vs. dew point generator LI-610. Dew points are in sequence set to 19°C, 1°C, 3°C, 5°C, 7°C, 9°C, 11°C, 13°C, 15°C, 17°C, 19°C for air mode and 18°C, 1°C, 4°C, 8°C, 12°C, 16°C, 18°C for N<sub>2</sub> mode. Fitting is polynomial function with constraint point of (0,0).

## 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 6 (left)). The calibration function can be well represented with a simple linear fit:  $y = x - 0.31$  (Figure 6 (right)).

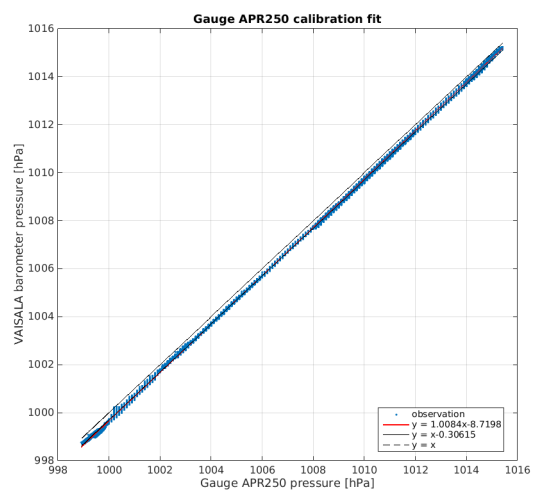
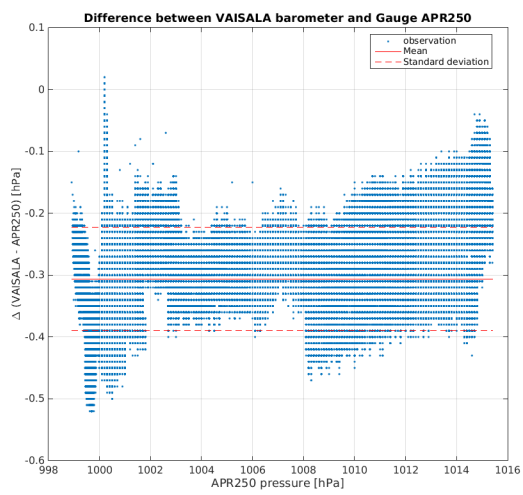


Figure 6: The discrepancy between the digital barometer (Vaisala) and the vacuum gauge (APR250) (left). The discrepancy is systematic and can be well represented with a simple linear fit:  $y = x - 0.31$ (right).