A dedicated robust instrument for water vapor generation at low humidity for use with a laser water isotope analyzer in cold and dry polar regions.

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Abstract

Obtaining precise continuous measurements of water vapor isotopic composition in dry places (polar or high-altitude regions) is an important challenge. The current limitation is the strong influence of humidity on the measured water isotopic composition by laser spectroscopy instruments for low humidity levels (below 3000 ppmv). This problem is addressed by determining the relationships between humidity and measured δ¹⁸O and δD of known water standards. We present here the development of a robust field instrument able to generate water vapor, down to 70 ppmv, at very stable humidity levels (average 1σ lower than 10 ppmv). This instrument, operated by a Raspberry interface, can be coupled to a commercial laser spectroscopy instrument: it turned to be very stable in an autonomous mode during more than one year at the East Antarctic Concordia station.

1. Introduction

The recent development of laser spectroscopy instruments now enables the continuous measurement of the isotopic composition of water vapor at many observation stations all around the world (Bailey et al., 2015; Bastrakov et al., 2014; Schmidt et al., 2010; Sodemann et al., 2017; Tremoy et al., 2011). In particular, the isotopic composition of the water vapor has proven to be a very useful tool to document moist synoptic events in many locations (Bonne et al., 2014; Guilpart et al., 2017). In polar regions, the water vapor isotopic signal is not only useful to detect the origin of moist air (Bréant et al., 2019; Kopec et al., 2014) but also to improve the interpretation of the isotopic composition of water in surface snow and ice core archives (Steen-Larsen et al., 2014). Indeed, exchanges are occurring after deposition between the surface snow and the water vapor leading to modifications of the isotopic composition of the former and hence of the archived ice (Casado et al., 2016, 2018; Ritter et al., 2016).
Obtaining continuous measurements of the water vapor isotopic composition at Concordia station in central Antarctica is a key scientific challenge since the deep ice core drilled there, EPICA Dome C, provides the oldest continuous water isotopic record to date (Jouzel et al., 2007). It is thus a key reference for the study of past climate, and a correct interpretation of the isotopic record relies on the quantification of the transfer function between climate parameters and water isotopic composition in ice, itself influenced by exchanges with water vapor in the upper layers of the firm (Casado et al., 2018). Such knowledge is also of uttermost importance for the interpretation of water isotope records from the starting deep drilling project “Beyond EPICA-Oldest Ice” (https://www.beyondepica.eu), whose aim is to drill a 1.5-million-year old ice core on the Little Dome C site located 40 km away from Concordia station, hence with similar low temperature and humidity conditions.

One of the main limitations of the current commercial instruments when deployed in polar regions is their relatively poor performance at low water vapor concentration. Generally, the precision of the measured isotopic ratios $\delta^{18}O$ and $\delta D$ rapidly worsens when the water mixing ratio decreases to humidity levels below 3,000-5,000 ppmv (part-per-million per volume) (Bonne et al., 2014; Weng et al., 2020). However, in remote continental areas in Greenland and Antarctica, temperatures in winter can drop to very low values, leading to humidity levels down to 10 ppmv (Genthon et al., 2017). Arguably one of the most extreme experiments for continuous measurement of the water vapor isotopic composition was probably the deployment of a commercial Picarro L2130-i instrument at the East Antarctic French-Italian station of Concordia where the mean annual temperature is around -54°C and the humidity barely exceeds 1000 ppmv during the warmest summer days (Casado et al., 2016). For such applications, there are two major impacts of low humidity on the raw isotopic signal: first, we generally observe an apparent increase in the $\delta^{18}O$ and $\delta D$ with decreasing humidity level and second, the standard deviation associated with the continuous measurements of $\delta^{18}O$ and $\delta D$ of the water vapor increases. It can thus lead to overall uncertainties of several % for $\delta^{18}O$ and tens of % for $\delta D$. It is thus of uttermost importance to have a correct determination of the humidity dependency of the water vapor isotopic ratios.

Commercial instruments from Picarro Inc. are usually associated with a Picarro Standard Delivery Module (SDM) dedicated to generate humidity at stable levels between 5,000 and 30,000 ppmv. Using such a setup for humidity levels below 5,000 ppmv leads to large uncertainties in the determination of the humidity influence on the water vapor isotopic composition (e.g. Guilpart et al., 2017). These uncertainties are due both to the instability of the water vapor generation using the SDM (in terms of water concentration – humidity— and/or isotopic composition) and due to the analytical noise in the spectroscopy measurements when the absorption signals are weak. An alternative commercial device is the LGR (Los Gatos Research) calibration system (water vapor isotope standard source, WVISS), which uses a nebulizer to instantaneously evaporate micro-droplets of liquid water from a standards reservoir into a large (1 L)
vaporizing chamber (Dong and Baer, 2010) This system is very stable and well adapted for humidity range between 2,500 and 25,000 ppmv (Aemisegger et al., 2012). Several home-made water vapor injection systems have been developed with the specific aim to achieve a better stability of the generated humidity at low humidity levels. A first approach is to use a dew point generator injecting small amounts of water into dry air (Lee et al., 2005; Wang et al., 2009). This approach is time consuming to reach equilibrium and relies on a very precise knowledge of the temperature to calculate the isotopic fractionation. A method using a piezoelectric microdroplet generator into a dry air stream could generate water mixing ratios at humidity levels between 12 and 3,500 ppmv (Iannone et al., 2009; Sturm and Knohl, 2009). However, adjustment of humidity level and long-term stability were difficult to obtain with such devices. Systems relying on the use of syringe pumps were also built by Gkinis et al. (2010) and Tremoy et al. (2011): a small fraction of the input stream of liquid water is introduced into a hot oven where water is vaporized in the presence of a dry air flow. These systems cover humidity range between 2,000 and 30,000 ppmv. Finally, bubbler systems, in which dry air flows through a large volume of water to create saturated vapor, are very robust but can only produce water vapor at high humidity level (Ellehoj et al., 2013). The aforementioned devices are unfortunately not well suited for automatic long-term operation at low humidity levels. During the 2014-2015 summer field season at Concordia station in Antarctica, a home-made humidity generator specifically designed for low humidity levels (Landsberg, 2014) has been deployed (Casado et al., 2016). The device used dual high-precision, low-volume, syringe pumps to generate stable humidity levels at two different isotopic compositions over the range from 100 to 800 ppmv (Casado et al., 2016). Unfortunately, we observed quite a large scattering among the isotopic values measured at similar humidity levels, as well as a large discrepancy between the humidity dependency of the water isotopic ratios measured in the field and that measured in the laboratory. Upon return to the laboratory, these defaults were traced primarily to tiny leaks in the water supply lines to the syringes. Therefore, we re-engineered the prototype by Landsberg (2014) in order to develop a robust and autonomous device for stable low level humidity generation for the purpose of precise humidity calibration of spectroscopic instruments. This device has now been operating with minimum manual intervention for more than one year at two polar stations in Antarctica, Dumont d’Urville and Concordia, coupled to Picarro laser spectroscopy instruments. We detail here the technical description of the instrument and show key performance characteristics, enabling, for instance, a discussion of small amplitude signals such as the diurnal variability of the water vapor isotopic composition in remote dry sites in East Antarctica.

2. New vapor generator for low humidity levels
The low-humidity level generator (LHLG) developed here relies on the same principle as the one developed by Landsberg (2014), i.e., a steady, undersaturated evaporation of a liquid water droplet at the tip of a needle into a dry air stream inside a small evaporation chamber. Based on this first prototype, the instrument has been remodeled including a specific hardware and software design.

2.1 Physical principle

The LHLG is based on undersaturated evaporation of a small droplet at the tip of a needle (Figure 1). Liquid water is pushed through a needle around which dry air is flowing. Dry air is obtained from a bottle of high purity synthetic air with pressure regulation through two manometers connected in series. The mass flux of water \( f_L \) is kept low compared to the air mass flow \( f_A \) so that the relative humidity \( h \) of the downstream moist air flow remains low (\( h < 0.1 \)). Therefore, the air stays largely undersaturated and its humidity is controlled only by the flow of liquid water in the needle and that of the dry air upstream of it. The mixing ratio (or humidity) of the air as classically provided by a Picarro instrument is given by:

\[
MR = \frac{d_{H2O} \times f_L \times R \times T_{st}}{f_A \times P_{st} \times M_{H2O}}
\]

where \( d_{H2O} = 1000 \text{ kg.m}^{-3} \) is the density of water, \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \) is the universal gas constant, \( T_{st} = 293.15 \text{ K} \) and \( P_{st} = 1.0 \times 10^5 \text{ Pa} \) are standard conditions of temperature and pressure and \( M_{H2O} = 18 \times 10^{-3} \text{ kg.mol}^{-1} \). Note that the flow of water \( f_L \) needs to be expressed in \( \text{m}^3.\text{min}^{-1} \) and the air flow \( f_A \) is expressed in \( \text{m}^3.\text{min}^{-1} \) at 20 °C and 1 atm (standard cubic meter per minute).

Figure 1: Evaporation of a droplet in the humidity generator chamber: left, picture from the prototype from Landsberg (2014); right, schematics of the water molecules being transferred to the air flow (Casado, 2016).

Physically, when the flux of water or air is changed, there is first a transient regime during which the radius of the droplet changes, modifying the evaporative surface and therefore the humidity of the outgoing air.
Once a stationary regime is reached, the radius of the droplet is stabilized and the humidity is given by equation 1. In this regime, there is no accumulation of water molecules in the system and therefore the isotopic composition of the vapor produced is equal to the isotopic composition of the liquid water injected in the needle: \( R_V = R_L \) (note that because of the fractionation during the transition phase, the isotopic composition of the droplet \( R_D \) is necessarily different from \( R_L \) and \( R_V \)).

When changing the flux of evaporating water, we modify the size of the evaporating surface and therefore the radius of the drop. The evolution of the radius of the drop can be obtained from the resolution of a non-linear differential equation of the volume \( V \) of the drop:

\[
\frac{dV}{dt} = f_L - f_{evap} \tag{2}
\]

where \( f_{evap} = k_e \times S \) is the evaporation flux depending of \( k_e \), the evaporation rate and \( S \), the surface area of the drop exposed to the dry air. A good approximation is to consider the shape of the drop as a fraction of a sphere of variable radius intercepted by the surface of a disk of constant radius (the syringe tip). By solving numerically the differential equation (2), it is possible to faithfully simulate the behavior of the device under changing conditions. The isotopic composition is computed by the introduction of an evaporation fractionation factor following Cappa et al. (2003). This numerical approach validates the theoretical explanation of the undersaturated evaporation of the droplet. It is noted that in steady-state, the isotopic composition of the generated water vapor does not depend on the injected flux of water, nor on the specific humidity.

### 2-2- Instrument conception

- **Technical realization**

As the LHLG relies on operating in a stationary regime, it is important that the dry air input and the water input are steady. Thus, the air and water fluxes, as well as the air pressure in the evaporation chamber are controlled by electronic PID regulators. The dry air flux is regulated by a high-precision mass flow controller (Vögtlin GSC-A9TS-DD22) operating at a range from 6 to 600 sccm (std cm\(^3\) min\(^{-1}\)) and an accuracy of 3.3 sccm. The water flux is regulated by a high-precision syringe pump (Harvard Apparatus Pump 11 Pico Plus Elite Dual), which can produce a water flow down to 10.8 pL min\(^{-1}\) with an accuracy of 0.35 % using syringes with a volume ranging from 10 µL to 250 µL. We operate in the routine mode with a dry air flow of 300 sccm and a water flow between 0.02 to 0.5 µL min\(^{-1}\) using mainly 50 or 100 µL syringes. A single pump is equipped with two syringes that provide two water flows into two evaporation chambers in parallel (Figures 2 and 3). Each syringe is connected to a water reservoir and to an evaporation chamber by a double 3-way liquid valve (Rheodyne MXX777603) switching from an “infuse” mode to a “refill” mode.
A major change to the instrument designed by Landsberg (2014) is the introduction of this double 3-way valve with leak tight connections and an internal volume of 1.9 µL. This modification is an important improvement as it enables automatic handling of the standards from a reservoir to the evaporation chamber with a robust connection, avoiding in particular potential air bubbles in the water flow. Indeed, the compressibility of air bubbles trapped in the water flow can lead to flow irregularities by amplification of small non-linearities in the progression of the syringe plunger. This will lead to non-steady state operation, which in turn creates artefacts in the humidity and isotopic composition, reducing the performance of the calibration device. In addition, the 3-way valve provides the opportunity of a "refill" mode in which the syringes draw standard water from a reservoir. When equipped with 100-µL syringes, the instrument can operate for several hours up to one day between refills. With the addition of the auto-refill option and the effective suppression of bubbles, the instrument can be used unattended for many months, as required for an Antarctic winter field campaign.

Figure 2: Humidity generator schematic diagram

The evaporation chambers are stainless steel cylinders equipped with specific connectors (Swagelok Ultra-Torr SS-4CD-TW-25) holding silicon rubber septa through which needles are inserted toward the middle of the chamber. The pressure in both chambers is regulated by a pressure controller (Bronkhorst P-702CV-1K1A-AAD-22-V) with a precision of 3 mbar in a range from 0 to 1,000 mbar. This pressurization of the two chambers combined with the relatively high flow (higher than required by the infrared spectrometers) enables maintaining a steady state whether or not the infrared spectrometer is connected, and increases the time efficiency of calibration procedures. The control of the instrument is ensured by a Raspberry Pi that can be interfaced to the L2130-i in sequencer mode (see below).
The hardware has been designed to meet the specifications dictated by field conditions: 1) All components are fixed in a transportable case (except the dry air bottle), isolated from vibration by an anti-vibration foam. 2) A panel of connectors (HDMI, USB, Ethernet, etc.) ensures the accessibility to the instrument when it is closed. 3) The electrical and electronic parts (e.g. power supply, Raspberry Pi) are separated from the rest of the instrument (e.g. sensors, gauges). Both the electrical and electronic parts are fully and easily accessible in case of failure.

**Figure 3:** Picture of the upper stage of the instrument with the main fluidic parts. Two water standards (A); a dual syringe pump (B); a double three-way valve (C); two evaporation chambers (D); an input of dry air (E); two high-precision mass flow controllers (F1 & F2); two electrovalves (G1 & G2); a pressure controller (H); an outlet (O).

- **Software details**

  The control software has been developed using open source Python libraries and homemade drivers, including a user interface displaying the state of relevant components and the value of the different sensors. The software (HumGen) can be downloaded on line (https://github.com/ojsd/humgen; https://doi.org/10.5281/zenodo.4003465).
The LHLG can operate in eight different states, each state representing a specific setup for each element (valves position, syringe pump infusion rate, dry air flow rate, pressure). Those eight states can be divided into three categories: a simple mode, an expert mode and a humidity dependence calibration mode. The simple mode is composed of six predefined states referring to the classical isotopic calibration in everyday routine operation (Table 1): 1) measurement of the outside air water vapor isotopic composition; 2) drying of the cavities; 3) “humidity boost”, in order to reach faster the desired humidity level in the cavities; 4) injection of the standard A in the corresponding evaporation chamber at a set humidity level; 5) injection of the standard B in the corresponding evaporation chamber; 6) refill of the syringes. The expert mode is useful to adjust each parameter manually: flow rates on the controllers F1 and F2, opening of the electrovalves G1 and G2, mode (injection or refill) and infused rate for the syringe pump, pressure regulation, state of the double three-way valve, activation of the vacuum pump at the exhaust, opening of external electrovalves from the dry air tank and to the inlet (Figures 2 and 3). The humidity dependence calibration mode produces a scale of increasing humidity steps in the evaporation chambers (e.g. from 100 ppmv to 1000 ppmv, through steps of 100 ppmv for 50 minutes for each standard). The details of the sequence (standard type, humidity level and duration of each step) is defined in a text file by the operator from the Raspberry interface, the Raspberry being itself connected to Ethernet for remote access.

The L2130-i analyser has an External Valve Sequencer, which is able to turn on/off up to six electrovalves and create loop sequences with defined durations for each step of the sequence. This tool can be diverted from its original purpose by using it as a 6-digit code: each of the humidity generator’s state is associated with a code. When the Picarro’s Valve Sequencer matches one of the state’s code, this state is triggered on the humidity generator. This eases both the operator’s activities and the data post-treatment, because the current valve status - thus the calibration instrument state - is saved in the analyzer output data file, in the "ValveMask" column. The Raspberry inside the LHLG reads the Valve Sequencer state code using the Picarro’s Remote Control Interface (a RS232 serial connection through one of the rear-face DB9 connector).

<table>
<thead>
<tr>
<th>States (min)</th>
<th>Flow F1 (sccm)</th>
<th>Flow F2 (sccm)</th>
<th>Valve G1</th>
<th>Valve G2</th>
<th>Syringe Pump (µL/min)</th>
<th>Inlet Valve *</th>
<th>Dry air valve</th>
<th>Pressure controller (mbar)</th>
<th>Pressure Pump for exhaust</th>
<th>Double 3-way valve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outside air (1100)</td>
<td>0</td>
<td>0</td>
<td>Closed</td>
<td>Closed</td>
<td>0</td>
<td>Open</td>
<td>Closed</td>
<td>Off</td>
<td>Off</td>
<td>To chamber</td>
</tr>
<tr>
<td>Drying (20)</td>
<td>400</td>
<td>400</td>
<td>Open</td>
<td>Open</td>
<td>0</td>
<td>Closed</td>
<td>Open</td>
<td>Off</td>
<td>Off</td>
<td>To chamber</td>
</tr>
</tbody>
</table>
Table 1: Typical routine sequence of measurements + calibration for two standards A and B at 1000 ppmv for a measurement site located at sea level.

Note that the humidity dependence mode and the expert mode can also be included in the valve sequencer but are not used in a daily calibration routine. *) The Inlet Valve is placed outside the vapor generator instrument; when open it enables the measurement of outside air.

A set of tools has been developed to quickly check daily calibration. In the field, analyzer and LHLG data are archived daily and sent to the laboratory, i.e. at LSCE, Gif sur Yvette. They are checked semi-automatically once a week to warn maintenance personnel in the event of a malfunction.

**3- Performance of the instrument**

The LHLG is able to generate stable levels of humidity ranging from 70 ppmv to 2300 ppmv.

**3-1- No fractionation during water vaporization in the cavity**

We have checked that there was no fractionation of the water during its transfer from the bottles to the the syringe pump, then from the syringe to the moist air generated in the vaporization chamber. The isotopic composition of three different standards have been compared, generated by the present LHLG as well as the commercial SDM, both at a humidity of 2,000 ppmv over 40-min time spans. The measured $\delta^{18}$O and $\delta^D$ excess values agreed to within 0.2‰ and 1‰, respectively, for the 3 standard waters. Note that 2,000 ppmv is close to the upper value of the present LHLG (2,300 ppmv) while it is the very low one of the SDM (see Fig. 6 of section 3-2).

**3-2- Stability of the water vapor delivery**

<table>
<thead>
<tr>
<th>Boost (0.7)</th>
<th>300</th>
<th>300</th>
<th>Open</th>
<th>Open</th>
<th>Infuse at 2.5</th>
<th>Closed</th>
<th>Open</th>
<th>905</th>
<th>On</th>
<th>To chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard A (50)</td>
<td>300</td>
<td>150</td>
<td>Open</td>
<td>Closed</td>
<td>Infuse at 0.25</td>
<td>Closed</td>
<td>Open</td>
<td>905</td>
<td>On</td>
<td>To chamber</td>
</tr>
<tr>
<td>Standard B (50)</td>
<td>150</td>
<td>300</td>
<td>Closed</td>
<td>Open</td>
<td>Infuse at 0.25</td>
<td>Closed</td>
<td>Open</td>
<td>905</td>
<td>On</td>
<td>To chamber</td>
</tr>
<tr>
<td>Reset (1)</td>
<td>Closed</td>
<td>Closed</td>
<td>Closed</td>
<td>Closed</td>
<td>Withdraw max speed</td>
<td>Open</td>
<td>Closed</td>
<td>Off</td>
<td>Off</td>
<td>From standard</td>
</tr>
</tbody>
</table>
Figure 4: Records of $\delta^{18}$O, $\delta^D$ and humidity over 3 humidity plateaus (72 ppmv on the left, 425 and 335 ppmv on the right) obtained with the LHLG (December 2018 at Concordia). The grey rectangles indicate the period (10 min) over which the average values are kept for calibrating the data generated by the L2130-i analyzer.

Figure 4 displays the performance of the instrument at different low humidity levels (72, 425, and 335 ppmv). In the routine mode, we select the last 10 minutes before the following switch of the instrument to measure the average level of humidity and the isotopic ratios, $\delta^{18}$O and $\delta^D$. We also calculate the associated standard deviations and reject the values if the humidity standard deviation exceeds 30 ppm over these last 10 minutes. In Figure 4, one observes that the standard deviations for humidities generated are actually much lower, in the 2 ppm range. The corresponding standard deviations for the isotopic ratios ($\delta^{18}$O and $\delta^D$, see values indicated in Figure 4) increase with decreasing humidity, reflecting the molecular absorption signal decrease recorded by the Li2130-i laser analyzer. This has an obvious impact on the determination of the relationship between humidity and water vapor isotopic composition.

The performance of the present LHLG can be compared to the performance of the SDM. For such comparison, we used daily calibrations performed with a SDM, in a routine mode, during a 4.5 years field deployment in Svalbard (Leroy-Dos Santos et al., 2020). Over the full series, we kept only the 10-minute plateaus where standard deviation associated with humidity variations during calibration was below 150 ppmv. The best result at low humidity over the full period was a standard deviation $\sigma$ of 31 ppmv over 10 minutes at 500 ppmv. Standard deviation largely increases when humidity decreases. This best SDM performance is significantly below the performance of the LHLG, which is a standard deviation $1-\sigma$ lower than 10 ppm on average and a $1-\sigma$ of 2 ppm for 30% of the generated humidity plateaus.

3-3- Determination of the influence of humidity on water vapor isotopic composition
Figure 5: Influence of humidity on the isotopic composition (δ18O and δD) of the vapor obtained with a SDM (red) and with our new LHLG (black). The error bars are calculated as the standard deviation (1 σ) over the generated values by the L2130-i instrument at 1 second resolution (i.e. without any pre-averaging of the raw dataseries). The δ18O ref and δD ref are the true values of the injected water standards.

Contrary to the commercial SDM, which hardly produces stable and reproducible humidity levels below 500 ppmv, the LHLG was able to daily produce stable 10-minute humidity plateaus over the range from 70 ppmv to 2,000 ppmv with an associated standard deviation lower than 10 ppmv over more than one year at the Concordia station (installation in December 2018). The stability of the LHLG allows a robust quantification of the L2130-i analyzer drift thanks to a daily measurement of the same water isotopic standard reference (Table 2). It also permits the characterization of the measurement nonlinearities observed at low humidity (Figure 5). The more than one-year long Concordia dataset showed that the humidity dependence of δ18O and δD did not vary measurably. The uncertainty of the obtained calibration curve can be attributed entirely to the L2130-i δ18O and δD measurements. In other words, the uncertainty bars in the horizontal (x-) axis for the black curve in Fig. 5, associated with the LHLG, are negligible.
### Table 2: Example of daily measurements of humidity (1σ over 10 minutes = 9 ppmv), $\delta^{18}$O (1σ over 10 minutes = 1.4 ‰), and $\delta$D (1σ over 10 minutes = 4.5 ‰) of a laboratory standard (NEEM) using the LHLG at low humidity during the austral summer of 2019-2020.

<table>
<thead>
<tr>
<th>Date</th>
<th>Humidity (ppmv)</th>
<th>$\delta^{18}$O (‰)</th>
<th>$\delta$D (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 December 2019</td>
<td>380</td>
<td>-32.0</td>
<td>-207</td>
</tr>
<tr>
<td>17 December 2019</td>
<td>369</td>
<td>-31.9</td>
<td>-210</td>
</tr>
<tr>
<td>23 December 2019</td>
<td>371</td>
<td>-31.7</td>
<td>-212</td>
</tr>
<tr>
<td>24 December 2019</td>
<td>367</td>
<td>-31.9</td>
<td>-211</td>
</tr>
<tr>
<td>25 December 2019</td>
<td>378</td>
<td>-31.7</td>
<td>-211</td>
</tr>
<tr>
<td>26 December 2019</td>
<td>370</td>
<td>-31.7</td>
<td>-209</td>
</tr>
<tr>
<td>27 December 2019</td>
<td>386</td>
<td>-32.3</td>
<td>-208</td>
</tr>
<tr>
<td>28 December 2019</td>
<td>370</td>
<td>-31.5</td>
<td>-211</td>
</tr>
<tr>
<td>29 December 2019</td>
<td>364</td>
<td>-31.5</td>
<td>-209</td>
</tr>
<tr>
<td>30 December 2019</td>
<td>380</td>
<td>-31.7</td>
<td>-211</td>
</tr>
<tr>
<td>31 December 2019</td>
<td>372</td>
<td>-31.8</td>
<td>-211</td>
</tr>
<tr>
<td>1 January 2020</td>
<td>379</td>
<td>-31.8</td>
<td>-212</td>
</tr>
<tr>
<td>2 January 2020</td>
<td>371</td>
<td>-31.7</td>
<td>-211</td>
</tr>
<tr>
<td>3 January 2020</td>
<td>381</td>
<td>-31.6</td>
<td>-210</td>
</tr>
<tr>
<td>4 January 2020</td>
<td>378</td>
<td>-31.6</td>
<td>-210</td>
</tr>
<tr>
<td>5 January 2020</td>
<td>371</td>
<td>-31.6</td>
<td>-208</td>
</tr>
</tbody>
</table>

4- **Application**

The main application of this device is the interpretation of water isotopic profiles at dry sites, in particular in polar regions. As shown in Figure 5, the influence of humidity on the measurement of the water vapor isotopic composition with the L2130-i analyzer is large when humidity is below 2,000 ppm and increases when humidity decreases. Even though the precise isotope ratio-humidity calibration curve is likely to be different from one analyzer to another, all laser-based water isotope analyzers investigated to date have shown a strongly non-linear response at low humidity levels (Guilpart et al., 2017; Leroy Dos-Santos, 2020; Weng et al., 2020). At the Concordia station, even in summer, humidity is generally below 1000 ppm (Figure 6) so that the interpretation of the diurnal variability of the water vapor isotopic composition is strongly affected by the dependency of the measured $\delta^{18}$O and $\delta$D signals on humidity. Figure 6 displays such diurnal variabilities during austral summer 2018-2019 at Concordia and the consequently large correction of the isotopic records (uncorrected in grey and corrected in black).
Figure 6: $\delta^{18}$O, $\delta^{D}$ and humidity records over December 2018 and beginning of January 2019. Raw isotopic values are in grey. Corrected isotopic values at hourly resolution are in black after correction of the influence of humidity on the water isotopic ratios and removal of measurements performed during calibration or other maintenance operations.

The data clearly demonstrate the importance of the humidity correction which shifts the curves generally to lower isotopic ratio values. However, the difference between uncorrected and corrected data is particularly important in the observation of the diurnal variability, illustrated even better when zooming in on a section of the data, as in Figure 7. When looking in detail at the diurnal variability in the raw $\delta^{18}$O and $\delta^{D}$ isotope data, some periods stand out with two daily peaks identified, one in phase with the humidity peak (marked in red in Figure 7) and one occurring during the period of minimum humidity (marked in blue in Figure 7). The strong non-linearity of the calibration curve of Figure 5 suggests that artificial peaks in $\delta^{18}$O and $\delta^{D}$ could be due to changing humidity levels. Indeed, after correcting the data for the humidity dependence of the analyzer (black curve in Figure 7), the isotopic peaks occurring during humidity minima are diminished or disappear altogether, while the peaks occurring during humidity maxima are amplified. More strikingly, the phase of the signal changes by practically 180° over some periods. Whereas the raw isotope signal peaks during the night, the corrected record shows higher isotope ratios during daytime. The diurnal variability recorded on both raw and corrected isotopic values during a period with higher humidity level, hence when the isotope ratio-humidity correction is smaller (around day 355 in figure 6), also shows that the $\delta^{18}$O ($\delta^{D}$) diurnal cycles are indeed in-phase with the humidity cycle. This result confirms the correlation between humidity cycles and $\delta^{18}$O and $\delta^{D}$ of the water vapor at the daily scale at Concordia as reported by Casado et al. (2016). We thus conclude that the anticorrelation...
observed between $\delta^{18}$O ($\delta D$) and humidity in the raw data (highlighted in blue in Figure 7) during periods of low humidity is an artefact due to the influence of the humidity level on the vapor isotopic measurements by the L2130-i analyzer.

**Figure 7**: Focus on diurnal variability of $\delta^{18}$O, $\delta D$ and humidity recorded at Concordia. Grey curves show the raw measurements and black curves the corrected records. The red (blue) bars indicate the calculated uncertainty due to the isotopes vs humidity dependence (Figure 5) on the corrected $\delta^{18}$O and $\delta D$ values during periods with maximum (minimum) humidity. The red (blue) rectangles indicate half day with maximum (minimum) humidity.

5- **Conclusion**

We have developed an autonomous instrument for low humidity generation (70 to 2,300 ppmv) with controlled water vapor isotopic composition specifically aiming at carrying out continuous measurements of the water vapor isotopic composition using a laser-based spectrometer in regions characterized by very low humidity, such as polar regions. An interface permits to conveniently connect the new LHLG to the valve sequencer port of commercial Picarro instruments. After more than one year of routine operation on two Antarctic sites (Dumont d’Urville and Concordia), this instrument has proven to be very reliable and robust. It consistently generates stable humidity levels with a $1\sigma$ variability lower than 10 ppm over more than 10 minutes. Besides, its performance is significantly better than that of the Picarro SDM at low humidity.
We used this instrument for the calibration of our water isotopic data with a special focus on accurately quantifying the influence of humidity on the measured isotopic composition of the water vapor. This effect is huge at low humidity. We showed that this has an important impact on the interpretation of the diurnal cycles of $\delta^{18}$O and $\delta^{2}$H in the water vapor at the Concordia station at humidity below 1,500 ppmv. We were able to confirm that, at this site, the diurnal $\delta^{18}$O and $\delta^{2}$H variability is actually correlated with humidity variability, which would not have been possible without the new LHLG instrument.

Finally, the development of such an instrument is an important step forward to a better understanding of the transfer function between climate parameters and the isotopic composition of deep ice cores from the remote East Antarctic plateau, especially in the context of the new program “Beyond EPICA”. It should be completed by ongoing development of laser spectrometers better adapted to low humidity levels, such as those based on the technique of Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS) (Casado et al., 2016; Landsberg, 2014; Landsberg et al., 2014).

**Author contributions**

CLDS, MC, FP and EK designed and built the instrument. OJ realized the software interface development. CLDS, MC and AL installed the instrument in Antarctica and tested it extensively. EK, SK and EF tested the instrument in the laboratory. AL wrote the manuscript with the help of all co-authors.

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