Second reply to the Editor’s comments

We would like to thank the Editor for his constructive comments which we have addressed below. We keep the editor’s comments in red font and our replies in black font.

Dear authors,

Thank you for having addressed all different requests in your revised version of your manuscript.

Please find below a list of minor remarks. I also would like to ask you to include an equation that gives your measurand (O2/N2 or p(O2)/p) as a function of measured quantities and calibration gases. This is crucial to evaluate the influence of different parameters on the overall measurement uncertainty and it also avoids misconceptions due to a purely "textual" explication.

Minor comments

L 34 : exponent for year.
Now corrected as yr\(^{-1}\)

L 35 : Suggestion : Write "Atmospheric O2 is commonly expressed in units of per meg due to its small variability with respect to a large background, where ..."

This phrase is now re-written as:

“Atmospheric O\(_2\) is commonly expressed in units of per meg due to its small variability with respect to a large background, where..”

L 42 - 43: I don’t think that one can understand the phrase "Note that we convert per meg to parts per million equivalent by multiplying per meg by 0.209500 (the O2 mole fraction of atmospheric air)." Did you eventually mean "Note that we convert delta (O2/N2) values (in per meg) to mole fractions (in ppm) using the conversion factor 0.209500 (the O2 mole fraction of atmospheric air)."? This is misleading. If I have delta = 0 per meg using the atmospheric ratio as a standard, I should have a mixing ratio of 0.209500 ppm. If I follow your description and multiply 0 by 0.209500, I get 0. It is preferable that you give an equation that unambiguously converts between the (dry) air mixing ratio and the delta values. The dry air mixing ratio clearly involves noble gases, CO2 and other minor components, whereas delta (O2/N2) does not ... I don’t see how one can easily convert by a fixed number.

Regarding the conversion or proportionality between per meg and ppm levels, please have a look at either of the following Webpages.

Regarding zero per meg: This means that the sample corresponds to the standard ratio and since N2 is constant in the atmosphere (except changes due to seasonal temperature changes of the ocean), that the O2 of the sample corresponds to the O2 of the standard. Therefore, no deviation in O2 which corresponds indeed to zero ppm change.

See https://cdiac.ess-dive.lbl.gov/trends/oxygen/modern_records.html
The units of $\delta$(O2/N2) are per meg; one per meg is one molecule of oxygen out of a million molecules of oxygen. Currently, this is roughly one molecule out of 4.77 million molecules of all gases in the atmosphere, not including water vapor molecules. Thus, 4.8 per meg is roughly one in a million molecules of dry air, or one part per million (ppm).

See http://scrippso2.ucsd.edu/faq

How does one relate ppm and per meg units?

These units refer to different types of quantities, so the question needs to be sharpened before it can be clearly answered. Suppose a tree consumes exactly one molecule of CO2 for each O2 molecule produced by photosynthesis. The changes in atmospheric O2 and CO2 near the tree will then be inversely proportional. What is the proportionality factor in per meg/ppm?

The answer is $1/0.2095 = 4.8$ per meg/ppm, where 0.2095 is the O2 mole fraction of air. This can be derived realizing that, because N2 is constant, the relative change in the O2/N2 ratio is the same as the relative change in O2 and calculating the relative change requires dividing by its abundance.

Therefore, the proportionality factor between per meg/ppm is

$4.77$ per meg = 1 ppm

1 per meg $= 1 / 4.77$ ppm $= 0.209500$. The latter number corresponds to the O2 mole fraction of air.

Actually, from eq. 1 you can easily see the proportionality if N2 is assumed to stay constant (fair assumption see above) and further write O2 of the sample as O2 of standard plus DO2. Resolving to DO2 yields the mentioned proportionality between per meg and ppm.

Also, please provide a reference for your value of 0.209500.

We have now provided the reference Machta and Hughes, 1970.

L 104: measurement wavelength -> wavelength measurement.

Now corrected accordingly

P 10 : As mentioned previously, the AFGL codes 161 and 162 are used exactly twice in the whole document (apart from the definition). Given that a large part of AMT readership has no spectroscopic background it is preferrable to use the more commonly known notation H2O and HDO (or the IUPAC definition) or the words "normal and deuterated water" at these instances. It has to be admitted that the AFGL notation is very handy for all people used to it.

We have now removed the AFGL codes and used H2O and HDO

L 151+: Phrase appears twice.

The repeated phrase is now removed

L 257 : I could not find the word "centration" in the dictionary. Do you mean "line centre position", perhaps?
It is now corrected as “line center position”

L 260 : correct the exponent in wavenumber unit

It is now corrected as cm\(^{-1}\)

L 305 : Not clear what is meant by "the correlation may be due in part to the fitting procedure itself". You might need to explain a little bit more, even though a reference is given. I suspect (but I am not sure) that you speak about the choice of variables for the fitting function (rather than the procedure or the algorithm). For example, the width and the line area are necessarily correlated, whereas width and absorption depth are likely less correlated.

The editor’s comments are correct. We meant to say that covariance of the width and area could be part of the explanation for the observed correlation. We now replaced “due in part to the fitting procedure itself” with “due in part to covariance of the fitted amplitude (proportional to line area) and line width”.

L 267 : HITRAN gives a value gamma_H2O = 0.0514 cm\(^{-1}\)/atm, which seems to come from semi-empirical calculations : https://arxiv.org/abs/1906.01475 . Please mention and check origin of that number.

We have now modified the paragraph from 265-272 as follows:

“From the linear fit one obtains a coefficient for collisional broadening of the Q13Q13 line by water vapor of \(\gamma_{\text{water}} = 0.0442 \text{ cm}-1\text{/atm at 45 °C} \). Recently, parameters describing broadening of oxygen lines by water vapor, obtained by empirical modeling of selected experimental data, were added to the Hitran data base (Tan et al., In review). The new Hitran entries predict a value of 0.0486 cm-1/atm at 45 °C, which is in agreement with our measurement within the 5-10% uncertainty attributed by Hitran to the broadening parameter.”

L 311 : "because the O2/N2 and water concentration", add "ratio" after "O2/N2" and "the" before "water concentration"

It is now corrected and read as:

“..., because the O2/ N2 ratio and the water concentration affect the line width...”

L 329 : "normalizing absorption amplitudes to line widths does not provide any advantage". It is difficult to understand what is meant here. Could you please clarify further ? Do you mean normalising amplitudes by line widths ?

Yes, we mean normalizing amplitudes by line widths

We now replaced “to” with “by”

L 333 : Perhaps you should remove the word "Consequently" here. (As a reply to your comment on a similar and previous remark, please consider that the reader does not necessarily have Fig 1 at hand and in mind when comparing to the 16O2 absorption. Also, the noise level is not evident from that figure 1,
as residuals usually reflect systematic effects such as bias in the profile, fringes, etc. some of which might scale with the size of the absorption line).

We have now removed the word “Consequently”

L 381 : write "tau is the averaging time" and use the greek symbol instead of the word "Tau"

The sentence in bracket is now modified as follows:

(t is the averaging time which is the abscissa of the Allan-Werle plot).
High-precision atmospheric oxygen measurement comparisons between a newly built CRDS analyzer and existing measurement techniques

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Abstract

Carbon dioxide and oxygen are tightly coupled in land-biospheres CO₂ - O₂ exchange processes, while they are not coupled in oceanic exchange. For this reason, atmospheric oxygen measurements can be used to constrain the global carbon cycle, especially oceanic uptake. However, accurately quantifying the small (~1-100 ppm) variations in O₂ is analytically challenging due to the very large atmospheric background which constitutes about 20.9% (~209500 ppm) of atmospheric air. Here we present a detailed description of the analyzer and its operating principles as well as comprehensive laboratory and field studies for a newly developed high-precision oxygen mixing ratio and isotopic composition analyzer (Picarro G-2207) that is based on cavity ring-down spectroscopy (CRDS). From the laboratory tests, we have calculated a short-term precision (standard error of one-minute O₂ mixing ratio measurements) of < 1 ppm for this analyzer based on measurements of eight standard gases analyzed for two hours consecutively. In contrast to the currently existing techniques, the instrument has an excellent long-term stability and therefore a calibration every 12 hours is sufficient to get an overall uncertainty of < 5 ppm. Measurements of
ambient air were also conducted at the High-Altitude Research Station, Jungfraujoch and the
Beromünster tall tower in Switzerland. At both sites, we observed opposing and diurnally
varying CO₂ and O₂ profiles due to different processes such as combustion, photosynthesis
and respiration. Based on the combined measurements at Beromünster tower, we determined
height dependent O₂:CO₂ oxidation ratios varying between -0.98 to -1.60, which increase
with the height of the tower inlet, possibly due to different source contribution such as natural
gas combustion with high oxidation ratio and biological processes which are at the lower end.

1. Introduction

Atmospheric oxygen comprises about 20.9% of the global atmosphere and in the past decade
its concentration decreased at a rate of ~20 per meg yr⁻¹ (Keeling and Manning, 2014) mainly
associated with the increase in fossil fuel combustion. Measurements of atmospheric O₂ are
reported as the ratio to the N₂ concentration and expressed as δ(O₂/N₂) because the variations
in the concentrations of other atmospheric gases such as CO₂ can influence the O₂ partial
pressure while this ratio is insensitive to these changes in other gases. Atmospheric These
variations in atmospheric O₂ is commonly expressed in units of per meg due to its small
variation variability with respect to a large background, where

\[
δ\left(\frac{O₂}{N₂}\right)\text{ (per meg)} = \left(\frac{\frac{O₂}{N₂}\text{sample}}{\frac{O₂}{N₂}\text{reference}} - 1\right) \times 10^6 \quad (1)
\]

Note that we convert per meg to parts per million equivalent by multiplying per meg by
0.209500 (the O₂ mole fraction of atmospheric air) (Machta and Hughes, 1970).
In contrast to O₂, the global average atmospheric CO₂ mixing ratio increased to 405.0 ppm
averaged over 2017 since its preindustrial value of 280 ppm (Le Quéré et al., 2017). As the
variability of atmospheric oxygen is directly linked to the carbon cycle, both its short and
long-term observations can be used to better constrain the carbon cycle. For example, since
first suggested by Keeling and Shertz (1992) the long-term trends derived from concurrent
measurements of atmospheric CO\textsubscript{2} and O\textsubscript{2} have been widely used to quantify the partitioning
of atmospheric CO\textsubscript{2} between the land-biosphere and oceanic sinks (Battle et al., 2000; Goto et
al., 2017; Manning and Keeling, 2006; Valentino et al., 2008). This method hinges on the
linear coupling between CO\textsubscript{2} and O\textsubscript{2} with an oxidation ratio (OR, defined as the
stoichiometric ratio of exchange during various processes such as photosynthesis and respiration
expressed using α\textsubscript{r} of 1.1 for the terrestrial biosphere photosynthesis-respiration processes
(α\textsubscript{r}) and 1.4 for fossil fuel combustion (α\textsubscript{f}) while they are decoupled for oceanic processes (α\textsubscript{o} = 0). Meanwhile, the short-term variability in atmospheric oxygen can be used to estimate
marine biological productivity and air-sea gas exchange (Keeling et al., 1998; Nevison et al.,
2012). However, the accuracy of these estimates is primarily linked to the accuracy and
precision of atmospheric O\textsubscript{2} measurements and the assumed ORs for the different processes
which are highly variable in contrast to atmospheric CO\textsubscript{2} that can be well measured within the
precision guidelines set by the Global Atmospheric Watch (GAW) (± 0.1 ppm for the
northern hemisphere).

Currently there are several, mostly custom built techniques that can measure
atmospheric O\textsubscript{2} variations as oxygen concentration based on interferometric, paramagnetic,
UV absorption and fuel cell technology (Keeling, 1988a; Manning et al., 1999; Stephens et
al., 2007) or as O\textsubscript{2}/N\textsubscript{2} ratios to account for the large background effect using gas
chromatography with thermal conductivity detector (GC-TCD) or gas chromatography
coupled to mass spectrometry (GC-MS) (Bender et al., 1994; Tohjima, 2000). Despite the fact
that these techniques have been used for more than two decades, accurate quantification of
atmospheric oxygen variability remains challenging primarily because the small ppm-level
atmospheric oxygen signal rides on a ~ 210,000 ppm background, which places stringent
requirements on the precision and drift of the analysis methods especially for continuous monitoring (note that the GAW recommendation for the measurement precision of O$_2$/N$_2$ is 2 per meg). The techniques listed above struggle to routinely achieve the necessary performance for various reasons, including i) instability over time that requires frequent measurement interruption for calibration, ii) measurement bias with ambient and sample temperature and/or pressure, and/or iii) systematic errors in the measurement due to other atmospheric species. Further, some techniques require the use of consumables and rely on high vacuum, which complicates field deployment.

In this manuscript we describe a new high precision oxygen concentration and isotopic composition analyzer by Picarro Inc., Santa Clara, USA (G-2207) based on CRDS technology. Here, we will introduce the analyzer design principles in details, describe the unique features of the analyzer and evaluate its performance based on various independent laboratory and field tests by comparing it with currently existing techniques. Then, we will present and interpret our observations based on field measurements. Finally, we will conclude its overall performance and provide recommendations and possible improvements.

2. Analyzer design principles

The analyzer described here is derived from the Picarro G2000 series of CRDS analyzers. The basic elements have been described elsewhere (Crosson, 2008; Martin et al., 2016; Steig et al., 2014): briefly, the instrument is built around a high-finesse, traveling-wave optical cavity, which is coupled to either of two single-frequency Distributed FeedBack-stabilized semiconductor lasers. One cavity mirror is mounted on a piezoelectric translator (PZT) to allow fine tuning of the cavity resonance frequencies. A semiconductor optical amplifier between the laser sources and the cavity boosts the laser power and serves as a fast-optical switch. The cavity body is constructed of invar and enclosed in a temperature
stabilized box (T = 45° C, stabilized to approximately 0.01 °C) for dimensional and spectroscopic stability. A vacuum pump pulls the gas to be sampled through the cavity and a proportional valve between the cavity and the pump maintains the sample pressure in the cavity at a value of 340 hPa, with variations on the order of 1 Pa. The instrument has a wavelength monitor, based upon measurements of interference fringes from a solid etalon, which is used to control the laser wavelength by adjusting the laser temperature and current. The wavelength monitor is a fiber-coupled device located between the laser and the cavity. A fraction of the beam from the input fiber is collected using a beam splitter for the wavelength measurement and the remaining power is collected in the output fiber. A high-speed photodiode monitors the optical power emerging from the cavity. The instrument’s data acquisition system is used to sweep the laser frequency over the spectral feature to be measured, modulates the laser output to initiate ring-downs, and fits the ring-down signal to an exponential function to generate a spectrogram of optical loss versus laser frequency. For this instrument the empty cavity ring-down time constant is about 39 μs. Subsequent program modules compare the measured loss spectrum to a spectral model, using non-linear least-squares fitting (Press et al., 1986) to find the best-fit model parameters and thereby obtain a quantitative measure of the absorption due to the target molecule, and finally apply a calibration factor to the optical absorption to deduce the molecular concentration. When operating in its normal gas analysis mode, the instrument acquires about 200-300 ring-downs per second and achieves a noise equivalent absorption of typically about $10^{-11}$ cm$^{-1}$ Hz$^{-1/2}$, with some variation between instruments.

The primary goal when designing this analyzer was to measure the molecular oxygen concentration with few-per-meg level precision and stability. In this context operational stability is as important as signal-to-noise. Our experience has been that the most stable
operation of the analyzer is achieved when the optical phase length of the cavity is held as
nearly constant as possible. In this case the free spectral range (FSR, 0.0206 cm⁻¹) of the
temperature stabilized, invar ring-down cavity provides a better optical frequency standard
than the etalon-based wavelength monitor, which in turn allows more consistent
measurements of absorption line width and integrated absorption line intensity (Steig et al.,
2014). For a small, field-deployable instrument, it is not practical to stabilize the absolute
frequencies of the cavity modes to an optical frequency standard (Hodges et al., 2004) but the
oxygen lines themselves, under conditions of constant temperature and pressure, provide an
adequate frequency reference. The oxygen spectrum was also used to calibrate the FSR, by
comparing a wide (approximately 10 cm⁻¹) FSR-spaced spectrum with the Hitran database
(Rothman et al., 2013).

To determine molecular oxygen concentration, the analyzer measures absorption of the
Q₁₃ component of the a¹Δg ← X¹Σg⁻ band, at 7878.805547 cm⁻¹, according to the latest
edition of Hitran (Gordon et al., 2017). This is one of the strongest near-infrared lines of
oxygen, well separated from other oxygen lines, and reasonably free of spectral interference
from water, carbon dioxide, methane, and other constituents of clean air. The spectral model
for this line was developed using reference spectra of clean, dry, synthetic air that were
acquired with the same hardware as in the field-deployable analyzer, but with special-purpose
software that allows it to operate as a more general spectrometer.

Recently, considerable work has been done to advance the understanding of spectral
line shapes and to define functional representations that better describe the processes that
determine spectral line shapes than does the Voigt model (Hartmann et al., 2008; Tennyson et
al., 2014, Tran et al., 2019). Line shape studies have been published for the 1.27 μm band of
O₂ (Fleisher et al., 2015; Lamouroux et al., 2014), though not to our knowledge for the Q
branch. The apparatus used here is not capable of spectroscopic studies of comparable precision; the absolute temperature and pressure monitoring and especially the frequency metrology are far too crude for that purpose. Our goal is merely to define a simple model of the Q13Q13 line that is adequate for least-squares retrievals of the O$_2$ absorption under the limited range of conditions (stabilized temperature and pressure) that the operational analyzer experiences in the field. The CRDS analyzers use the Galatry function (Varghese and Hanson, 1984), which is distinctly better than the Voigt and still easily and quickly evaluated for line shape modeling. Ultimately, the usefulness of the spectral model is to be evaluated by the precision and stability of the O$_2$ measurements when compared with established techniques.

Ultimately, the usefulness of the spectral model is to be evaluated by the precision and stability of the O$_2$-measurements when compared with established techniques. For spectral model development, this spectrometer has the drawback that the cavity FSR, is too large to reveal much detail of the absorption line shape, even with the simplifying assumption of a Galatry line shape. We therefore acquired a set of four interleaved spectra, with the PZT-actuated mirror moved to offset the cavity modes of the individual FSR-spaced spectra by one-fourth of an FSR. The precise offsets were determined from fits to the strong and well-isolated O$_2$ lines in the spectra. From the consistency of the fitted line centers, we estimate that the positioning of the interleaved spectra was accurate to approximately 10 MHz. The spectrum of the Q13Q13 line acquired in this manner is shown in Figure 1, together with the best-fit Galatry function. It stands out that the residuals are largely odd in detuning from the line center: this shows the limitations of the Galatry model in this case, since the Galatry function is purely even about the line center. The shape of the absorption line in this model is specified by two dimensionless parameters: the collisional broadening parameter

$$\gamma = \frac{\gamma}{\sigma_D}$$

(2)
and the collisional narrowing parameter

\[ z = \frac{\beta}{\sigma_D} \]  

(3)

where \( \gamma \) is the frequency of broadening transitions, \( \beta \) is the velocity change collision rate, and \( \sigma_D \) is the 1/e Doppler half-width of the transition, given by

\[ \sigma_D = v_0(2k_B T/M c^2)^{1/2} \]  

(4)

where \( v_0 \) is the transition frequency, \( k_B \) is Boltzmann’s constant (J K⁻¹), \( T \) is the sample temperature (K), \( M \) is the molecular mass (amu), and \( c \) is the speed of light (m/s). Figure 2 shows the values of \( y \) and \( z \) obtained from spectra acquired in the same way as Figure 1, as a function of cavity pressure. The values depend linearly on pressure, as expected from the Galatry model, but the unconstrained linear fits do not go precisely through the origin. It is not clear whether this represents a breakdown of the Galatry model or simply reflects the limited quality of the data set. The slope of \( y \) can be converted to an air-broadened collisional width \( \gamma_{\text{air}} = 0.0442 \text{ cm}^{-1}/\text{atm} \), which agrees with the Hitran value of 0.0460 cm⁻¹/atm (Gordon et al., 2016) to within the uncertainty estimate stated by Hitran (uncertainty code 4 for \( \gamma_{\text{air}} \) corresponding to 10% --20% relative uncertainty). The slope of \( z \) can be interpreted in terms of the optical diffusion coefficient (Fleisher et al., 2015), yielding \( D = 0.285 \text{ cm}^2 \text{ s}^{-1} \), compared to the literature value of 0.233 cm² s⁻¹ for \( \text{O}_2 \) in air at 45 °C (Marrero and Mason, 1972).

Although the anticipated use of the analyzer is for ambient air samples having a very small range of \( \text{O}_2 \) concentrations, we did investigate the variation of the line shape in binary mixtures of \( \text{O}_2 \) and \( \text{N}_2 \) shown in Figure 3. The error bars are taken from the output of the Levenberg-Marquardt fitting routine (Press et al., 1992). The dependence of the collisional broadening parameter \( z \) on \( \text{O}_2 \) mole fraction was considered too small to be significant, but the variation in \( y \) was used in the subsequent analysis of the air samples. Note that Wójtewicz
et al. (Wójtewicz et al., 2014) also found collisional broadening coefficients for nitrogen to be slightly larger than for oxygen in measurements of one O$_2$ line in the B-band.

The primary goal in designing the analyzer was to achieve high enough precision to make meaningful measurements of O$_2$ in clean atmospheric samples. Although the current best practice for such high-precision measurements is to work with dried samples, we decided to include high precision measurements of water vapor. There were two reasons for this decision: one is to serve as a monitor for residual water vapor, which is difficult to remove completely from the ring-down cavity and associated sample handling hardware, and the second and more ambitious reason was to see how well the effect of water vapor could be corrected for measurements of undried ambient air. While it was considered unlikely that measurements of undried air could compete in accuracy with those of dried air, it might be possible to correct for water vapor well enough to enable useful measurements in some circumstances without the expense and inconvenience of drying the sample. For this purpose, a second laser was added, which probes the $7_{1,6} \rightarrow 8_{4,5}$ component of the $2v_3$ band of water vapor, at of 7816.75210 cm$^{-1}$ (Gordon et al., 2017). The Galatry model was used to fit spectra of synthetic air humidified to various levels of water vapor concentration. These fits also included two other nearby, very weak water lines, with intensities less than 1% of the strong transition, in order that their absorption should not perturb the line shape of the main transition. Results for the shape of the 7816.75210 cm$^{-1}$ line are shown in Figure 4. At the level that we can measure, only the y-parameter has a meaningful variation with water concentration. From the linear fit one obtains a pressure broadening coefficient for air, $\gamma_{\text{air}} = 0.0752$ cm$^{-1}$/atm, in reasonable agreement with the Hitran value $\gamma_{\text{air}} = 0.0787$ cm$^{-1}$/atm (Gordon et al., 2017), and a self-broadening coefficient $\gamma_{\text{self}} = 0.413$ cm$^{-1}$/atm, to be compared
with the Hitran value $\gamma_{\text{Hitran}} = 0.366$ cm$^{-1}$/atm. Since the uncertainty estimate for the Hitran values is 10% to 20%, this level of agreement seems reasonable.

We also looked at absorption from water near the Q13Q13 absorption line of $\text{O}_2$. These spectra were measured in a background of pure nitrogen to reveal the very weak lines interfering with the $\text{O}_2$ measurement. Without the strong $\text{O}_2$ lines, it was impossible to interleave FSR-spaced spectra, so in this case the frequency axis comes from the analyzer's wavelength monitor. The upper panel of Figure 5 shows the spectrum of saturated water vapor in nitrogen, together with a fit to a Voigt model of the molecular lines. The measurement was made at a pressure of 340 hPa and temperature of $45^\circ\text{C}$. The main features are the Q13Q13 line from trace contamination of oxygen in the sample and several lines that arise from normal water ($^{1}\text{H}_2^{16}\text{O}$, AFGL code 161) and deuterated water ($^{1}\text{H}^{2}\text{H}^{16}\text{O}$, AFGL code 162, also abbreviated HDO). The lower panel of Figure 5 shows the lines tabulated in Hitran. Immediately after the data in Figure 5 were acquired, measurements were also made at 7816.85210 cm$^{-1}$, to establish the relationship between the absorption strengths in the two spectral regions. The relative intensities of the $^{161}\text{H}_2\text{O}$ and $^{162}\text{HDO}$ lines change with variations in the isotopic composition of the water, but fortunately the direct interference with the oxygen Q13Q13 lines comes entirely from the $^{161}\text{H}_2\text{O}$ isotopologue, with the strongest $^{162}\text{HDO}$ line being separated by approximately 8 line widths (FWHM) from the Q13Q13 line. Hitran simulations for molecules other than water that are expected to be present in clean, ambient air indicate that direct interference with the Q13Q13 line should be negligible at the level of precision considered here. In the case of $\text{CO}_2$, the dilution of oxygen due to 400 ppm of $\text{CO}_2$ is significant, and larger than any direct spectral interference.

Finally, we investigated the influence of water vapor on the shape of the $\text{O}_2$ Q13Q13 line. Switching between the two lasers sources, we acquired FSR-spaced spectra of
humidified synthetic air, alternately covering the 7817 cm$^{-1}$ and 7878 cm$^{-1}$ regions. Individual spectra were acquired in less than 2 s, so changes in water vapor concentration between spectra were small. These spectra, with frequency resolution of 0.0206 cm$^{-1}$, were analyzed by nonlinear least-squares fitting with the following spectral models: the 7817 cm$^{-1}$ spectra were modeled as the sum of an empty-cavity baseline having an adjustable offset level and slope and the water spectrum is modeled with three peaks: one strong line and two weak perturbers. The molecular absorption of the main peak was expressed as an adjustable amplitude, $A_w$, multiplying a dimensionless, area-normalized Galatry function (Varghese and Hanson, 1984). The weak perturbers were modeled by Voigt profiles with amplitudes and line widths that were constrained to be in fixed proportions to the strong line, and therefore added no new degrees of freedom to the fitting procedure. Since the amplitude $A_w$ multiplies an area-normalized shape function, it is essentially equivalent to the area of the absorption line, to the extent that the Galatry model provides a valid description of the line shape. The Doppler width of the Galatry function was fixed based on the measured cell temperature, the $y$-parameter was allowed to vary, and the $z$-parameter was constrained to be proportional to $y$, based on measurements summarized in Figure 2. In addition, the center frequency of the Galatry function was adjusted to match the data set, giving a total of five free parameters for this fit. The 7878 cm$^{-1}$ spectra were modeled with an adjustable baseline offset and slope and molecular absorption amplitude, $A_{O_2}$, describing the Q13Q13 O$_2$ line. Here, too, the $y$-parameter and center position of the O$_2$ lines were allowed to adjust, and the $z$-parameter was constrained to be proportional to $y$. The weak water lines interfering with oxygen absorption were included in the model, but with no additional free parameters; rather the amplitudes were preset based on the measured water absorption at 7817 cm$^{-1}$ and the previously determined amplitude relationships between the water lines. This procedure does
not account for variations in HDO abundance, which may introduce some systematic error
into the water vapor correction for samples of unusual isotopic composition, but it should
accurately model the most important lines that interfere with the oxygen measurement.
Collisional broadening of the Q13Q13 O₂ line by water vapor is shown in Figure 6. From the
linear fit one obtains a coefficient for collisional broadening of the Q13Q13 line by water
vapor of γ_{water} = 0.0442 cm⁻¹/atm at 45 °C. We are not aware of previous measurements of
this quantity. Recently, parameters describing broadening of oxygen lines by water vapor,
obtained by empirical modeling of selected experimental data, were added to the Hitran data
base (Tan et al., In review). The new Hitran entries predict a value of 0.0486 cm⁻¹/atm at
45 °C, which is in agreement with our measurement within the 5-10% uncertainty attributed
by Hitran to the broadening parameter.

The alternating measurements at 7817 cm⁻¹ and 7878 cm⁻¹ also calibrated the
relationship between water mole fraction and the absorption at 7817 cm⁻¹, using a dilution
analysis described by Filges et al. (2018), who showed that the results obtained this way agree
well with water vapor fractions measured with a conventional hygrometer. Figure 7 shows the
measured amplitudes of the water and oxygen lines for samples of variable humidity. Since
the air came from a tank of constant composition, the oxygen concentration changes due to
dilution of oxygen when water is added. Assuming that this is the sole cause of the change in
measured absorption, since the line shapes were being constantly adjusted to account for
changes in collisional broadening, it is straightforward to deduce the relation between the
water fraction and the absorption amplitude. This calibration was used to generate the water
fraction axes in Figures 4 and 6. We note that we did not take particular care to control or
measure the quantity of dissolved gases, especially oxygen and carbon dioxide, in the water
used for this experiment. While these gases would not significantly affect the water
calibration, they may affect the water vapor correction of the oxygen measurement at the ppm level. More work needs to be done to investigate the water vapor correction of the oxygen measurement.

The observations described above were used to design a method to measure oxygen concentration in ambient air. Gas from the inlet to the analyzer is drawn through the cavity at a rate of about 100 sccm (standard cubic centimeter per minute) and the conditions in the cavity are held stable at 340 hPa and 45°C. In its analysis mode the analyzer alternately measures ring-downs in the 7817 cm\(^{-1}\) and 7878 cm\(^{-1}\) regions. At 7878 cm\(^{-1}\) measurements are made at 11 different frequencies, spaced by one FSR of the cavity and centered at the peak of the Q13Q13 line. Multiple ring-down measurements are made to improve the precision of the loss determination, with a total of 305 ring-downs allocated to one spectrum. In the 7817 cm\(^{-1}\) region measurements are also made at 11 distinct frequencies at FSR spacings. Only 35 ring-downs are allocated to this spectral region, since the measurement of O\(_2\) is much more important than water vapor. The data sets are analysed using a Levenberg-Marquardt fitting routine, which adjusts five free parameters in each region to find the best agreement to a spectral model based on Galatry line shapes, as described above. One of the outputs of the 7878 cm\(^{-1}\) fit is the frequency offset of the FSR grid from the center of the Q13Q13 line. This information is used to adjust the position of the PZT actuated mirror to keep the measurements centered on the line, effectively stabilizing the optical path length of the cavity to the frequency of the O\(_2\) line. The reported water fraction is obtained by multiplying the fitted amplitude of the water line by a calibration constant derived from the dilution experiment as explained above. For the O\(_2\) fraction a slightly more complicated procedure is followed. It was observed that the least-squares fitting of the data gives highly correlated results for the amplitude of the absorption line and the line width parameter y. The correlation
may be due in part to the fitting procedure itself (Press et al., 1992) and it may also have a contribution from pressure variations that the pressure sensor is unable to detect. The ratio $A_{O_2}/y$ can be determined from the fit much more precisely than $A_{O_2}$ alone and so gives a more sensitive measurement of molecular absorption. It also has the advantage of being independent of sample pressure, to the extent that the Galatry model applies (Figure 2).

However, using the ratio $A_{O_2}/y$ as a metric for absorption adds more complications if measurements are to be made over a range of $O_2$ and water concentrations, because the $O_2/N_2$ ratio and the water concentration affect the line width independently of pressure and $O_2$ concentration alone. To minimize systematic errors due to these broadening effects, we define a nominal $y$-parameter based on the measured amplitudes of the $O_2$ and water lines and the line broadening dependences shown in Figures 3 and 4. The measured ratio $A_{O_2}/y$ is normalized by the nominal $y$ to obtain a quantity that is ideally independent of pressure and water concentration, and this is the quantity that is multiplied by a calibration constant to give the reported $O_2$ fraction. In addition, a dry mole fraction is reported for $O_2$, defined as the directly measured mole fraction corrected for water dilution.

The main goal in developing this instrument was to make high precision measurements of $O_2$ mole fraction, based on absorption by the dominant $^{16}O_2$ isotopologue. The absorption lines of the rarer isotopologues are also present nearby, so a mode of operation was included in which one laser is scanned over neighboring lines of $^{16}O_2$ and $^{16}O^{18}O$ and the ratio of amplitudes is used to derive an isotopic ratio, reported in the usual delta notation. In this case the operating pressure was reduced to 160 hPa to improve the resolution of the nearby lines. The lines measured were the Q3Q3 line of $^{16}O_2$, at 7882.18670 cm$^{-1}$, and the Q9Q9 line of $^{16}O^{18}O$, at 7882.050155 cm$^{-1}$. The measurement procedure is very much like
that for the O\textsubscript{2} fraction measurement, so it will not be described in detail, only the main
differences will be noted. One is that in determining an isotopic ratio, normalizing absorption
amplitudes to line widths does not provide any advantage, instead we simply take the ratio
of amplitudes to compute delta. Although the Q9Q9 line and its neighbor Q8Q8 are the
strongest ones in this band, absorption by 16O\textsuperscript{18}O is still very weak, only about 5x10^{-9} \text{ cm}^{-1} at
the line center under the conditions we used. Consequently, the signal-to-noise that can be
achieved with this analyzer is not adequate to determine both the amplitude and the width of
the 16O\textsuperscript{18}O line with useful precision, so in the fitting step the y-parameter of the 16O\textsuperscript{18}O line
is constrained to be a constant factor times the fitted y-parameter for the 16O\textsubscript{2} line.
Additionally, because of the weakness of the rare isotopologue absorption, the majority of
ring-downs in each spectrum is devoted to measuring 18O\textsuperscript{16}O i.e. 232 ring-downs in each
spectrum versus only 40 for 16O\textsubscript{2}. This implies that the mole fraction measurement in the
isotopic mode is much less precise than when the analyzer measures the Q13Q13 line alone.

3. Results and Discussions

3.1. Laboratory tests at Picarro, Santa Clara

3.1.1. Temperature and pressure sensitivity

One set of tests was done to determine how well the goal was met of minimizing the
susceptibility of the concentration measurements to noise or drift of the sample temperature
and pressure. For these tests the analyzer sampled dry synthetic air from a tank and the
temperature and pressure setpoints of the cavity were adjusted upward and downward from
the nominal values, to obtain an estimate of the differential response. We express the
sensitivity to experimental conditions in relative form, that is the derivative with respect to
temperature or pressure divided by the signal under nominal conditions.
From these experiments, we determined a temperature sensitivity of $-2.1 \times 10^4$ K$^{-1}$ and a pressure sensitivity of $+9.8 \times 10^4$ hPa$^{-1}$. The temperature sensitivity is somewhat larger than expected based on a calculation using Hitran data to estimate the temperature dependences of all the quantities that go into the measured absorption of the Q13Q13 line. The pressure sensitivity is strikingly small, indicating a good cancelation of the pressure dependence of absorption amplitude and line width. Both temperature and pressure sensitivities are small enough to have a negligible effect on short-term precision of measurements made with the stabilized ring-down cavity, though long-term drifts in the sensors are always a matter of concern.

3.1.2. Measurement precision and drift

Measurement precision was evaluated by analyzing synthetic air containing nominal atmospheric concentrations of CO$_2$ and CH$_4$ from an aluminum Luxfer cylinder over a period of several days. The tank, oriented horizontally and thermally insulated (though not controlled), was connected directly to the instrument (S/N TADS2001) with a 2-stage pressure regulator and stainless-steel tubing with an additional orifice to about 55 sccm. For the isotopic mode of operation, the precision of the measurement was also tested by making repeated measurements from a tank of clean, dry synthetic air.

Figure 8 shows the time series of the precision test data, displaying the reported oxygen concentration, the height of the oxygen absorption peak, the width of the oxygen absorption peak and the ambient temperature. The residual error of the analyzer, although small, is nevertheless significant given the stringent targets set forth by the WMO-GAW program. Possible sources of error include: temperature drifts due to sensor drift or gradients; pressure errors due to sensor drift; optical artifacts such as parasitic reflections, higher order
cavity mode excitation, and/or loss nonlinearity that can distort the reported oxygen spectrum. More work is required to identify and eliminate these small drifts.

The Allan standard deviation of the reported O₂ fraction is shown in the Allan-Werle plot in Figure 9. The ordinate on this plot is the square root of the Allan variance of reported mole fraction, so 1 ppm in these units corresponds to about 5 per meg in the ratio of O₂/N₂. The precision of averaged measurements improves as $\tau^{-1/2}$ for approximately 5000 s and reaches 1 ppm in less than 10 minutes and remains below 1 ppm for time scales on the order of about 1 hour (the averaging time which is the abscissa of the Allan-Werle plot).

Figure 10 shows the precision of $\delta^{18}$O (uncalibrated) derived from the ratio of lines measured at 7882 cm⁻¹. Because of the weak signal from the $^{16}$O$^{18}$O line, it is necessary to average for more than 20 seconds or more to achieve 1‰ precision on the isotopic ratio. As for the concentration measurement, averaging improves the measurement precision for time scales up to about 1 hour.

3.2. Laboratory measurements at the University of Bern

3.2.1. Measurements of standard gases

The performance of the instrument was tested by analyzing eight standard gases with precisely known CO₂ and O₂ compositions (Table 1) using the CRDS analyzer and comparing it to parallel measurements with a paramagnetic oxygen sensor (PM1155 oxygen transducer, Servomex Ltd, UK) embedded to a commercially available fuel cell oxygen analyzer (OXZILLA II, Sable Systems International, USA) (Sturm et al., 2006) as well as with an isotope ratio mass spectrometer (IRMS, Finnigan DeltaPlus-XP). The design of the measurement set-up is shown in Figure 11. Standard gases were directly connected to the pressure controlling unit, and a multi-port valve (V2) was used to select among the standard gases. Flow from each cylinder was adjusted to about 120 sccm which was eventually...
directed to a selection valve (V1), allowing switching between ambient air and standard gases.

Flow towards and out of the fuel cell analyzer was controlled by the pressure controlling unit.

The O₂ mixing ratio of this incoming gas was first measured on the Paramagnetic O₂ sensor and then directed towards a non-dispersive infrared analyzer (NDIR) (Li-7000, LICOR, USA) for measuring CO₂ and H₂O. The outflow from this analyzer (100 sccm) returns to the pressure controlling unit and was eventually divided between the CRDS analyzer (which uses about 75-80 sccm) and the IRMS (~ 20 sccm) via a Tee-junction. Each cylinder was measured for two hours in each system controlled by a LabView program.

First, we investigated the influence of this Tee-junction, which splits the gas flow between the CRDS and the IRMS, on the measured O₂ values. Manning (2001) showed that the fractionation of O₂ in the presence of a Tee-Junction is strongly dependent on the splitting ratios as well as temperature and pressure gradients. Hence, we measured and compared the O₂ mixing ratios of two standard gases (CA07045 and CA060943) in two cases: i) in the presence of a Tee-junction with different CRDS to IRMS splitting ratios and ii) without a Tee-junction so that all gas flow is directed towards the CRDS analyzer. The splitting ratios in these test experiments vary from 1:1 to 1:100, and reversed to change the major flow direction either to the CRDS or the IRMS. Note that the experimental condition in this manuscript is with a 4:1 splitting ratio (i.e. ~ 80 sccm towards the CRDS analyzer and ~ 20 sccm towards the IRMS).

In the cases of the smaller splitting ratios (1:1, 1:4 and 4:1), which are relevant for the results presented in this study, only minor differences in the measured O₂ mixing ratios were observed when compared to case ii (i.e. without a Tee-junction). For these two cylinders measured, the average differences in these cases were about 0.5 ppm, calculated as the mean of the differences in the raw O₂ measurements of the last 60 seconds. The negligible
Fractionation can indeed be the result of smaller splitting ratios while strong influence is usually expected in case of larger splitting ratios (Stephens et al., 2007). For higher splitting ratios, the result seems inconclusive without any dependence on the ratios due to the strong decline in the cylinder temperature (specifically at the pressure gauge) caused by higher flow to achieve the higher splitting ratios (as high as 1:100). Hence, these tests need to be conducted in a temperature-controlled condition and the results could not be discussed in this manuscript.

Figure 12 shows the standard gas measurements for the seven cylinders with known CO₂ and O₂ mixing ratios (Table 1) using both the CRDS and the Paramagnetic analyzers. Standard eight, which has too high O₂, is not shown in the figure as the figure is zoomed-in to better illustrate the change in O₂ for the remaining cylinders. While the first five cylinders contain O₂ and CO₂ mole fractions comparable to ambient air values, standards 6 & 8 had either very low or very high O₂, respectively. In addition, standards 6 and 7 have very low and very high CO₂ mixing ratios. Note that due to its very high CO₂ content (~ 2700 ppm), standard 7 was not measured on the IRMS and hence the O₂ mixing ratio is unknown. The measured mixing ratios for the six standard gases measured with the two systems are in very good agreement while cylinder 7 showed an opposing signal for the two analyzers compared to standard 6 (Figure 12). While the Paramagnetic analyzer showed a higher O₂ mixing ratio, the values from the CRDS analyzer are lower in O₂. This can be associated with the very high CO₂ mixing ratio in standard 7, which leads to a strong dilution effect in the CRDS analyzer as it does not include any correction function for dilution effect from CO₂. However, such high CO₂ mixing ratios may not be that important for most atmospheric research. Yet, it should be considered to include a parallel CO₂ mixing ratios measurement to the instrument.
as it will further improve the accuracy. This would be especially important for biological or physiological studies where a wide range of CO₂ and O₂ concentrations must be expected. 

The measurement precision of the CRDS analyzer was calculated as the standard error of the mean i.e. the standard deviation (1-σ) of the last 1-minute raw measurements divided by the square root of the number of measurements (n = 60), and for all these cylinders the values are usually between 0.5 ppm to 0.7 ppm. For parallel measurements of these cylinders using a Paramagnetic analyzer, we obtained a precision of about 1 ppm, calculated exactly the same way.

We also made a correlation plot to see which of the two instruments are in better agreement with the assigned values based on IRMS measurements for the individual cylinders. While similar correlation coefficients were observed for both analyzers, different slopes were calculated (Fig. A.1). This is due to the fact that the IRMS measures the O₂ to N₂ ratio (δ(O₂/N₂)) in per meg, while the CRDS and the Paramagnetic analyzers provide non-calibrated O₂ mixing ratios in units of ppm and per meg, respectively. If we exclude the two standard gases with the highest and lowest O₂ mixing ratios (standards 7 and 8) that are subjected to strong dilution effects, both the slope and the r² values decrease from those shown in Figure A.1. But this decrease is larger in the case of the Paramagnetic measurements, implying a slightly better linearity of the CRDS analyzer.

3.2.2. Measurements of ambient air

Ambient air measurements were conducted from the roof top of our laboratory at the University of Bern to evaluate the analyzer’s performance under atmospheric variability. Ambient air was continuously aspirated from the inlet at the roof of the building at a flow rate of ~ 250 sccm which is then dried using a cooling trap kept at -90 °C towards the switching valve (V1) and measured in similar way to the standard gases as explained above. The
measurement values obtained here were compared with the parallel measurements by the Paramagnetic sensor to test the instruments stability and accuracy.

Figures 13 panels a &b show the 1-minute average ambient air measurements from the rooftop inlet by the Paramagnetic and the CRDS analyzers at the beginning of the testing period including standard gases measured every 12-hour. While the Paramagnetic analyzer seems to be stable, the CRDS analyzer showed a strong drift for an extended period. This can be due to unstable conditions in the CRDS measurement system as it started operating right after it was unpacked. Hence, we looked into temperature inside the instrument chassis and pressure records, which were stable within the manufacturer’s recommended range during this period. As the CRDS analyzer incorporates a water correction function, interference from this species should be well accounted. Even comparing the analyzer’s parallel water measurements to water measurements by the NDIR system such a drift was not observed. It should be noted that the two internal standard gases which were less frequently measured (every 12 hours) during this period were also drifting following similar pattern. This implies that the drift is associated with the analyzer. Interestingly, this pattern can be modeled using a polynomial function which can then be used to correct for the observed drift in the ambient air measurements. After applying a polynomial drift correction, we were able to fully accounted for the observed drift. However, the manufacturer decided to further investigate possible causes of this drift. After further improvements, we obtained the first commercial analyzer in September 2017 and repeated the above tests (Figure 13 c &d). No such drift was observed any more in the standard gases or in ambient air measurements.

We believe that the optical amplifier has caused the drift in the first system and not anymore included in the design of the product which produced a significant amount of broadband light that could fill the cavity (albeit with a low coupling coefficient), and would ring down with a
different (and generally much faster) time constant that the baseline loss of the cavity. However, the ringdown time on the peak of the oxygen line is just 10 microseconds, such that the broadband light might have distorted the single exponential decay of the central laser frequency, leading to the observed drift in the oxygen signal. However, we were not able to confirm this hypothesis.

3.2.3. Water correction test

Measurements of oxygen are reported as both wet (O$_2$, raw) and dry (O$_2$, dry) mole fractions by the CRDS analyzer as it also measures water vapor in parallel at its water absorption line (7817 cm$^{-1}$), and corrects for the dilution effect based on an inbuilt numerical function:

$$O_2,_{dry} = \frac{O_2,_{raw}}{1-f_{H_2O}}$$  \hspace{1cm} (5)

where $f_{H_2O}$ is the measured water mole fraction.

The efficiency of water correction by this function was assessed in two ways: i) by comparing the water vapor content in standard air measured by this analyzer with similar measurements by the NDIR analyzer and ii) by comparing the oxygen mixing ratios between non-dried ambient air measured and corrected for water dilution by the CRDS analyzer with dried air measured using a paramagnetic analyzer.

Figure 14 shows the water vapor content for standard gases measured continuously for two days by the CRDS and the NDIR analyzers. Note that the two data sets are manually fitted to each other as the measured water values by the NDIR analyzer are not calibrated. Based on this plot, the two analyzers are in very good agreement although there are small differences during very dry conditions (low water content).
Figure 15a shows the dried ambient air water measurements in both analyzers with frequent spikes due to valve switching while measuring standard gases. In the second case, where the water trap was by-passed and non-dried air was allowed to the CRDS analyzer keeping the dried air flow to the NDIR (Figure 15b), a clear increase in the water measurements in the CRDS analyzer can be observed. Here, it should be noted that there are no spikes in the water measurements of the CRDS analyzers as there are no standard gas measurements in between and the inlet is directly connected to the CRDS analyzer (Figure 11). Figures 15c & 15d show the difference in oxygen measurements of ambient air measured in both analyzers in the two cases stated above (note that the CRDS uses its built-in water correction function applying Eq. 5). The measurements of the Paramagnetic analyzer were scaled to ppm units by applying the correlation equation obtained from the six standard gas measurements of the two analyzers (Fig. A.1). Note that the CRDS measurements were corrected for the observed drift using the polynomial fit to the two standard gas measurements stated above.

In the first period of the measurement when both analyzers measured dried ambient air, the absolute differences between the 1-minute averages measured over two days by the two analyzers were mostly within 15 ppm (Figure 15c) and symmetrically distributed around zero (Figure 15e). However, when wet air was admitted to the CRDS analyzer and the in-built water correction was applied, a stronger variability was observed in the calculated differences (Figure 15d). This implies stronger short term variability in the CRDS analyzer measurement values (as nothing was changed for the Paramagnetic measurement system) when wet samples were analyzed. The more negative values in the differences (Figure 15f) can also be associated with overestimation of the O₂ mixing ratios by the CRDS originating from an
overestimated water correction. However, detailed evaluation of the analyzer’s water correction function is beyond the scope of this study.

3.3. Field Measurements

After a series of tests at University of Bern, we conducted multiple field measurements at the High Altitude Research Station Jungfraujoch and the Beromünster tall tower sites in Switzerland described below.

3.3.1. Tests at the High Altitude Research station Jungfraujoch

The High Alpine research station Jungfraujoch is located on the northern ridge of the Swiss Alps (46° 33’ N, 7° 59’ E) at an elevation of 3580 m a.s.l. It is one of the global atmospheric watch (GAW) stations well-equipped for measurements of numerous species and aerosols. The site is above the planetary boundary layer most of the time due to its high elevation (Henne et al., 2010; Zellweger et al., 2003). However, thermally uplifted air from the surrounding valleys during hot summer days or polluted air from the heavily industrialized northern Italy may reach at this site (Zellweger et al., 2003). The Division of Climate and Environmental Physics at the University of Bern has been monitoring CO₂ and O₂ mixing ratios at this site based on weekly flask sampling and continuous measurements since 2000 and 2004, respectively (Schibig et al., 2015). The CO₂ mixing ratio is measured using a commercial NDIR analyzer (S710 UNO R, SICK MAIHAK) while O₂ is measured using the Paramagnetic sensor (PM1155 oxygen transducer, Servomex Ltd, UK) and fuel cells (Max-250, Maxtec, USA) installed inside a home-built controlling unit. Similar to the comparison tests at the University of Bern, we have conducted parallel measurements between the CRDS analyzer and the paramagnetic cell at this high altitude site during 03 – 14 February 2017. The measurement of ambient air at the Jungfraujoch system is composed of sequential switching between low span (LS) and high span (HS) calibration gases followed by a target gas (T)
measurement (once a day) to evaluate the overall system performance and finally a working
gas (WG) measurement before switching back to ambient air.

Figure 16 (top panel) shows the calibrated 1-minute averaged O$_2$ mixing ratios
measured at this high altitude site in comparison with the Paramagnetic oxygen analyzer
already available at the site. Despite the strong variability observed during the measurement
period of 10-days by both analyzers, a very good agreement was observed between them.

Figure 16 (bottom panel) shows the absolute difference of 1-minute averages in
atmospheric O$_2$ measured at Jungfraujoch between the two analyzers which are mostly within
±5 ppm range (but sometimes going as high as ±10 ppm) without an offset. However, for
generally reported 10-minutes, half-hourly or hourly means these values correspond to < 1.5
ppm, < 1 ppm and < 0.65 ppm.

3.3.2. Tests at the Beromünster tall tower site

The Beromünster tower is located near the southern border of the Swiss Plateau, the
comparatively flat part of Switzerland between the Alps in the south and the Jura mountains
in the northwest (47° 11′ 23″ N, 8° 10′ 32″ E, 797 m a.s.l.), which is characterized by intense
agriculture and rather high population density. A detailed description of the tower
measurement system as well as a characterization of the site with respect to local
meteorological conditions, seasonal and diurnal variations of greenhouse gases, and regional
representativeness can be obtained from previous publications (Berhanu et al., 2016; Berhanu
et al., 2017; Oney et al., 2015; Satar et al., 2016). The tower is 217.5 m tall with access to five
sampling heights (12.5 m, 44.6 m, 71.5 m, 131.6 m, 212.5 m) for measuring CO, CO$_2$, CH$_4$
and H$_2$O using Cavity Ring Down Spectroscopy (Picarro Inc., G-2401). By sequentially
switching from the highest to the lowest level, mixing ratios of these trace gases were
recorded continuously for three minutes per height, but only the last 60 seconds were retained
for data analysis. The calibration procedure for ambient air includes measurements of
reference gases with high and low mixing ratios traceable to international standards (WMO-
X2007 for CO₂ and WMO-X2004 for CO and CH₄), as well as target gas and more frequent
working gas determinations to ensure the quality of the measurement system. From two years
of data a long-term reproducibility of 2.79 ppb, 0.05 ppm, and 0.29 ppb for CO, CO₂ and
CH₄, respectively was determined for this system (Berhanu et al., 2016).

Between 15.02.2017 and 02.03.2017, we have connected the new CRDS oxygen
analyzer in series with the CO₂ analyzer (Picarro G-2401) and measured the O₂ mixing ratios
at the corresponding heights. Similar to the CO₂ measurements, O₂ was also measured for
three minutes at each height. During this period, we have evaluated the two features (isotopic
mode and concentration mode) of the CRDS analyzer. In the isotopic mode, the CRDS
measures the δ¹⁸O values as well as the O₂ concentration while in concentration mode only
the latter was measured.

During the tests conducted at this tower site, we first evaluated the two operational
modes (concentration vs isotopic modes) of the CRDS analyzer. Ambient air measurements
on isotopic mode over a 4-days period showed a strong variability in the measured oxygen
mixing ratios and it was not possible to distinguish the variability in the O₂ mixing ratios
among the five height levels. The calculated 1-minute standard error for ambient air
measurements was as high as 10 ppm while a standard error of less than 1 ppm was
determined from similar measurements in the concentration mode. Additionally, comparing
the O₂ values between the two modes, frequent short time variation in ambient air O₂ (~ 200
ppm) was observed in the isotope mode measurements while the variation in the concentration
mode is significantly smaller (~ 30 ppm). This precision degradation is due to the weaker ¹⁸O
oxygen line used for the isotopic mode, and the fact that far more ring-downs are collected on
the rare isotopologue in isotopic mode. Hence, we have conducted the remaining test
measurements in concentration mode.

As this tower has five sampling height levels, we first followed three minutes of
switching per inlet level, which enables four measurements per hour at a given level.

However, we noticed hardly any difference among the different levels due to strong short
term variability in O₂ mixing ratios between the consecutive heights. Hence, we switched to a
longer sampling period of six-minutes per height. Figure 17 shows the diurnal CO₂ and O₂
variations at the lowest (12 m) and highest (212.5 m) sampling heights of the tower. These
two heights were selected simply to better illustrate the difference in the mixing ratios. The
CO₂ mixing ratios on the top panel show higher values at the 12 m inlet than the highest level
most of the day due to its closeness to sources except during the afternoon (11:00 - 17:00 UTC) when both levels show similar but decreasing CO₂ mixing ratios. This is due to
presence of a well-mixed planetary boundary layer (PBL) (Satar et al., 2016). The lag in CO₂
peak between the two height levels by about two hours indicates the duration for uniform
vertical mixing along the tower during winter 2017. The opposite variability patterns are also
clearly visible in the O₂ mixing ratios shown in the lower panel with a clear distinction
between the two height levels during early in the morning and in the evening while similar O₂
values were observed in the afternoon. These opposing profiles are expected as CO₂ and O₂
are linearly coupled with a mean oxidation ratio of -1.1 ± 0.05 (Severinghaus, 1995) for land-
biospheric processes (photosynthesis and respiration) and -1.44 ± 0.03 for fossil fuel burning
(Keeling, 1988b).

Table 2 shows the oxidation ratios derived as the slopes of the linear regression
between CO₂ and O₂ mixing ratios at the different height levels measured on 25 February
2017. Accordingly, height dependent slopes were observed with a slope of -0.98 ± 0.06 at the
lowest level, close to the biological processes induced slope but slightly lower than its mean value. For the highest level, we calculated a slope of \(-1.60 \pm 0.07\) a value close to fossil fuel combustion oxidation ratio. Note that depending on fossil fuel type the oxidation ratio can range between -1.17 and -1.95 for coal and natural gas, respectively (Keeling, 1988b). While the slopes derived for the two other levels (44.6 m and 131.6 m) show similar values between the highest and lowest height levels, possibly from mixed sources, the middle level showed a slightly higher slope than these two levels but still in the large range between the lowest and highest inlet heights.

3.4. Evaluation of the \(\delta^{18}O\) measurements

To further evaluate the analyzer’s performance in measuring stable oxygen isotopes, we conducted ambient air isotopic composition measurements as well as analyzed a standard gas without \(CO_2\) which has a known \(\delta^{18}O\) value. The choice of this \(CO_2\)-free air standard gas is twofold: one it has a known \(\delta^{18}O\) value and second as it has no interference from possible \(CO_2\) absorption band overlap. For this test three 0.5 L glass flasks were preconditioned and filled with this standard gas to ambient pressure. These flasks were attached before or after the water trap (Fig. 11) and measured similar to ambient air measurements. These measurements were then compared with \(\delta(^{18}O/^{16}O)\) values obtained by parallel measurements using our IRMS.

Figure 18 shows the \(\delta^{18}O\) values of ambient air from the roof top with three consecutive measurements of glass flasks filled with \(CO_2\)-free air in-between followed by a fourth flask filled with breath air. An excellent agreement was observed for measurements from both instruments for the three flasks filled with a standard gas. However, the fourth flask with breath air showed a signal opposite to the measurements by the IRMS. As breath air contains large amount of water and \(CO_2\) in addition to \(O_2\), which can possibly interfere with
the CRDS analyzer measurements, we have removed H$_2$O and CO$_2$ by using a cryogenic trap (-130 °C) and in an additional experiment using Schütze reagent to remove both CO and CO$_2$. However, we have not observed any improvement towards an agreement with the IRMS measurements. Therefore, any other gas component in the breath air must be relevant for the interference. Based on the absorption lines in the spectral range of the instrument (7878 cm$^{-1}$) retrieved from HITRAN database, we expect interference either from carbon monoxide (now excluded by the tests) or methane or VOCs including acetone, ethanol, methanol or isoprenes, all of which have been measured in breath air (Gao et al., 2017; Gottlieb et al., 2017; Mckay et al., 1985; Ryter and Choi, 2013; Wolf et al., 2017). Further investigations have to shed light on these interferences in order to take corresponding action to surpass these shortcomings in the isotope analysis based on cavity ring-down spectroscopy.

4. Conclusions

We have thoroughly evaluated the performance of a new CRDS analyzer which measures O$_2$ mixing ratios and isotopic composition combining laboratory and field tests. Even if a drift in the analyzer was observed at the beginning of this study, which can be easily corrected by calibration, the recent analyzers built by the manufacturer did not show such instrumental drift. However, prior tests are recommended to see the analyzer’s stability.

The T-split tests for the current measurement setup based on the measurements of two standard gases showed a difference within the measurement uncertainty. However, this effect may become significant while applying larger splitting ratios and we recommend conducting further experiments to accurately quantify this influence for larger splitting ratios.

We have observed a strong influence of dilution in the measured O$_2$ values during the presence of high CO$_2$ mixing ratios. Even if such an influence may not be critical for the present study, such an effect might be significant in other studies where higher CO$_2$ mixing
ratios might be present and we recommend following a correction strategy based on parallel
CO₂ measurements. This also applies for more accurate analysis.

The water correction applied by the instrument’s in-built function seems to sufficiently
correct for the water vapor influence. However, a larger variability of the difference was
observed between the CRDS analyzer and the Paramagnetic cell when dried samples were
used in both systems. This can possibly be due to an overcorrection by the water correction
function of the CRDS analyzer when dried samples were used. This is particularly true for the
very low water vapor range (< 100 ppm). We believe that it is important to further investigate
this issue and identify an improved water correction strategy.

Based on the analysis of O₂ mixing ratios in the concentration and isotopic modes, we
have observed a significant decrease in precision (about ten-fold) in the latter measurement
mode. The measured δ¹⁸O values for the standard air by the CRDS analyzer are in excellent
agreement with the IRMS values. However, such measurements for a breath air showed a
contrasting signal, possibly due to interference from other gases such as CH₄. Hence, we
recommend further investigation on such possible contaminants and how to possibly remove
them while conducting ambient air measurements. However, we believe that this analyzer can
be used for tracer experiments where artificially enriched isotopes are used to study biological
processes such as photosynthesis in plants using isotopically labelled CO₂ and H₂O.

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measurement system at the Beromünster tower was built and maintained by the CarboCount-
CH (CRSH2_136273) and IsoCEP (200020_172550) projects both funded by SNF.
List of Tables

Table 1. Assigned mixing ratios of standard gases used in this study and their corresponding values measured by the NDIR, CRDS and IRMS at the University of Bern. 1The assigned values are based on measurements from different institutions (University of Bern (UB), Scripps or NOAA, see column cylinder name). 2Measurements are on the Bern scale for CO₂ and O₂. The Bern scale is shifted by +550 ppm. 3Values on the Scripps scale.

<table>
<thead>
<tr>
<th>Cylinder name</th>
<th>Assigned CO₂ (ppm)</th>
<th>Assigned O₂ (per meg)</th>
<th>CO₂-IRMS (ppm)</th>
<th>O₂-IRMS (per meg)</th>
<th>O₂-Paramagnetic (per meg)</th>
<th>O₂-CRDS (per meg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-1 LUX3576-UB</td>
<td>427.47</td>
<td>-1026</td>
<td>427.47</td>
<td>427.59</td>
<td>-1026</td>
<td>-1070</td>
</tr>
<tr>
<td>ST-2 LK922131-UB</td>
<td>368.09</td>
<td>599</td>
<td>368.09</td>
<td>367.82</td>
<td>599</td>
<td>560</td>
</tr>
</tbody>
</table>
## Table 2. The CO$_2$ and O$_2$ correlation coefficients at the different height levels derived using the least square fit and the correlation coefficients ($r^2$). Uncertainties are calculated as standard error of the slope.

<table>
<thead>
<tr>
<th>Height</th>
<th>Oxidation Ratios (O$_2$:CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5 m</td>
<td>-0.98 ± 0.06 (0.48)</td>
</tr>
<tr>
<td>44.6 m</td>
<td>-1.29 ± 0.07 (0.50)</td>
</tr>
<tr>
<td>71.5 m</td>
<td>-1.49 ± 0.08 (0.47)</td>
</tr>
<tr>
<td>131.6 m</td>
<td>-1.23 ± 0.05 (0.55)</td>
</tr>
<tr>
<td>212.5 m</td>
<td>-1.60 ± 0.07 (0.61)</td>
</tr>
</tbody>
</table>
Figure 1. The top panel (a) shows the raw data (points) and the best-fit Galatry function (solid line). Residuals of the Voigt fit are shown in panel (b) and residuals of the Galatry fit are shown in panel (c).
Figure 2. Best-fit values for the Galatry parameters of the Q13Q13 line of O₂, as a function of pressure. The line broadening parameter y is represented by circles and the line narrowing parameter z by squares. The solid lines are linear fits to the measurements. The best-fit offset and slope are 0.0227 and 0.004082 hPa⁻¹ for y, and -0.0169 and 0.001424 hPa⁻¹ for z.
Figure 3. Galatry parameters of the Q13Q13 line of O$_2$ at 340 hPa and 45° C as a function of O$_2$ mole fraction in binary O$_2$ - N$_2$ mixtures. The linear fits to the data are $y = 1.417 - 0.023 \times f_{O_2}$ and $z = 0.481 + 0.085 \times f_{O_2}$. 
Figure 4. Galatry parameters of the 7816.75210 cm$^{-1}$ water line in air at 340 hPa and 45° C as a function of water mole fraction. Black points are from measurements and red lines are linear fits: $y = 1.7846 + 8.01 \times f_{H2O}$ and $z = 0.656 + 3.60 \times f_{H2O}$. 
Figure 5. Upper panel: spectrum of water in nitrogen (points) and fit to Voigt model (blue curve). Lower panel: Oxygen (green), normal water (blue), and deuterated water (red) lines in the 2016 Hitran data base.
Figure 6. Galatry collisional broadening parameter of the oxygen Q13Q13 line at 340 hPa and 45° C versus water mole fraction. Black points are from measurements and the red line is a linear fit: $y = 1.4109 + 0.467 f_{H2O}$. 
Figure 7. Measured absorption line amplitudes for oxygen and water vapor for water vapor mixing ratios ranging from nearly 0 to 0.025. Black points are from measurements and the red line is a linear fit: with intercept $7.78001 \times 10^{-6} \text{ cm}^{-1}$ and slope $-0.014807$. 
Figure 8. Time series from a measurement of a single tank over about a week. The four panels show the water-corrected oxygen concentration, the absorption peak loss minus the baseline loss, the measured Lorentzian broadening factor, and the ambient temperature (measured in the instrument housing), respectively. A windowed average of 300 seconds was applied to all four data sets.
Figure 9. Precision of O$_2$ mole fraction measured from a tank of synthetic air. Filled circles are measurements and the line shows the ideal $\tau^{1/2}$ dependence.
Figure 10. Precision of $\delta^{18}O$ measured from a tank of synthetic air. Filled circles are measurements and the line shows the ideal $\tau^{-1/2}$ dependence.
Figure 11. Schematics of the measurement system used to compare the Picarro analyzer with the Mass Spectrometer at Bern.
Figure 12. Comparison of oxygen mixing ratios for the seven standard gases measured using the CRDS analyzer (black) and the Paramagnetic sensors (red).
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Figure 18. Consecutive $\delta^{18}O$ measurements of a standard gas (CO$_2$-free air) filled into three flasks followed by measurement of breath air using the CRDS analyzer (top) and IRMS (bottom). These measurements were carried out in the middle of ambient air measurements.
Figure A.1. Correlations between the $O_2$ mixing ratios measured by the CRDS and Paramagnetic analyzers with the mass spectrometric measurements (uncalibrated values). The left panels are for all the cylinders measured (standards 1 to 8) while the right ones are after selecting standards 1-5.
References


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