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 O₂ is
commonly expressed in units of per meg due to its small variability with respect to a large
background, where

\[ \delta \left( \frac{O_2}{N_2} \right) \text{(per meg)} = \left( \frac{O_2}{N_2} \text{sample} \right) \left( \frac{O_2}{N_2} \text{reference} \right)^{-1} \cdot 10^6 \]  

(1)

Equation 1 is used to convert oxygen mole fraction changes expressed in ppm (as measured
by several techniques such as paramagnetic cell, UV-cell as well as the by the CRDS analyzer
presented here) into changes in δO₂/N₂. This is associated with the influence of dilution
effects on the mole fractions but not necessarily on the ratios. These conversion difficulties
and their expressions in uncertainties are discussed in the Appendix. In contrast to O₂, the
global average atmospheric CO$_2$ 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$_2$ and O$_2$ have been widely used to quantify the partitioning of atmospheric CO$_2$ 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$_2$ and O$_2$ with an oxidation ratio (OR, defined as the stoichiometric ratio of exchange during various process such as photosynthesis and respiration expressed using $\alpha$) of 1.1 for the terrestrial biosphere photosynthesis-respiration processes ($\alpha_b$) and 1.4 for fossil fuel combustion ($\alpha_c$) while they are decoupled for oceanic processes ($\alpha_o = 0$). 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$_2$ measurements and the assumed ORs for the different processes which are highly variable in contrast to atmospheric CO$_2$ that can be well measured within the precision guidelines set by the Global Atmospheric Watch (GAW) ($\pm$ 0.1 ppm for the northern hemisphere).

Currently there are several, mostly custom built techniques that can measure atmospheric O$_2$ 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$_2$/N$_2$ 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 O2/N2 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 $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ 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 O₂ 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 O₂ 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 O₂ 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
\[ y = \gamma / \sigma_D \] (2)
and the collisional narrowing parameter
\[ z = \beta / \sigma_D \] (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
\[ \sigma_D = \nu_0 (2k_B T/Mc^2)^{1/2} \] (4)
where \( \nu_0 \) 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 cm\(^2\) s\(^{-1}\) for 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 O\(_2\) concentrations, we did investigate the variation of the line shape in binary mixtures of O\(_2\) and 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 $O_2$ 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, $\gamma_{air} =$
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 $\gamma_{\text{self}} = 0.366$ 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 O$_2$. These spectra were measured in a background of pure nitrogen to reveal the very weak lines interfering with the O$_2$ measurement. Without the strong 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° C. The main features are the Q13Q13 line from trace contamination of oxygen in the sample and several lines that arise from normal water ($^{1}$H$_2^{16}$O) and deuterated water ($^{1}$H$^{2}$H$^{16}$O 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 H$_2$O and 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 H$_2$O isotopologue, with the strongest 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 CO$_2$, the dilution of oxygen due to 400 ppm of 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, $A_{\text{O}_2}$, describing the Q13Q13 $\text{O}_2$ line. Here, too, the y-parameter and line center position of the $\text{O}_2$ 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 O\(_2\) 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 \(\gamma_{\text{water}} = 0.0442\) cm\(^{-1}\)/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. 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 covariance of the fitted amplitude (proportional to line area) and line
width (Press et al., 1992) and it may also have a contribution from pressure variations that the
pressure sensor is unable to detect. The ratio \( A_{O2}/y \) can be determined from the fit much more
precisely than \( A_{O2} \) 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 \( A_{O2}/y \) 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 \( A_{O2}/y \) is multiplied 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\(_2\) 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 by 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 $^{16}\text{O}^{18}\text{O}$ is still very weak, only about $5\times10^{-9}$ cm$^{-1}$ at the line
center under the conditions we used. The signal-to-noise that can be achieved with this
analyzer is not adequate to determine both the amplitude and the width of the $^{16}\text{O}^{18}\text{O}$ line with
useful precision, so in the fitting step the y-parameter of the $^{16}\text{O}^{18}\text{O}$ line is constrained to be a
constant factor times the fitted y-parameter for the $^{16}\text{O}_2$ line. Additionally, because of the
weakness of the rare isotopologue absorption, the majority of ring-downs in each spectrum is
devoted to measuring $^{16}\text{O}^{18}\text{O}$ i.e. 232 ring-downs in each spectrum versus only 40 for $^{16}\text{O}_2$.
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 $-2.1\times10^{-4}$ K$^{-1}$ and
a pressure sensitivity of $+9.8\times10^{-6}$ 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 $O_2$ 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 $O_2/ N_2$. 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 ($\tau$ is 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 CO$_2$ and O$_2$ 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 Delta$^{\text{Plus}}$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
carried out 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.

Furthermore, the slope between the IRMS and CRDS O₂ values in Figure A1 corresponds to 5.78 per meg ppm⁻¹, significantly larger than the conversion factor of 4.78 per meg ppm⁻¹ as derived from equation 1 assuming constant N₂ content. This higher slope is due to dilution effect originating from any gas component change (Delta, given in ppm) on all air components of air samples, which has not been corrected for the CRDS values. When accounting for this dilution effect - which scales with 1/(1+Delta), the factor approaches 4.78 per meg ppm⁻¹. The scaling of dilution effects is independent on which air component is changing and it affects all air components relative to their molecular fractions similarly. O₂
values on a CRDS or paramagnetic cell instrument is affected even if there is no change in O₂ or N₂ but only in CO₂ or water vapor or any other component which is present. This is in contrast to measurements of O₂/N₂ ratios for the same case where equal ratio would be measured. Major dilution influences are expected from O₂, CO₂ and H₂O changes due to natural exchange processes on air samples or when using artificial air-like compositions.

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 ($O_2,_{\text{raw}}$) and dry ($O_2,_{\text{dry}}$) mole fractions by the CRDS analyzer as it also measures water vapor in parallel at its water absorption line ($7817 \text{ cm}^{-1}$), and corrects for the dilution effect based on an inbuilt numerical function:

$$O_{2,\text{dry}} = \frac{O_{2,\text{raw}}}{1-H_2O} \quad (5)$$

where $H_2O$ 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 measurements (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 UNOR, SICK MAIHAK) while O₂ is measured using the Paramagnetic sensor (PM1155 oxygen transducer, Servomex Ltd, UK) and fuel cells (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 O₂ 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 O₂ 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 CO$_2$ and WMO-X2004 for CO and CH$_4$), 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, CO$_2$ and CH$_4$, 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 CO$_2$ analyzer (Picarro G-2401) and measured the O$_2$ mixing ratios at the corresponding heights. Similar to the CO$_2$ measurements, O$_2$ 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 $\delta^{18}$O values as well as the O$_2$ 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 $O_2$ 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 $O_2$ values between the two modes, frequent short time variation in ambient air $O_2$ ($\sim 200$ ppm) was observed in the isotope mode measurements while the variation in the concentration mode is significantly smaller ($\sim 30$ ppm). This precision degradation is due to the weaker $^{16}O$ 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 $O_2$ mixing ratios between the consecutive heights. Hence, we switched to a longer sampling period of six-minutes per height. Figure 17 shows the diurnal $CO_2$ and $O_2$ 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 $CO_2$ 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 $CO_2$ mixing ratios. This is due to presence of a well-mixed planetary boundary layer (PBL) (Satar et al., 2016). The lag in $CO_2$ 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 ± 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 δ¹⁸O 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 CO₂ which has a known δ¹⁸O value. The choice of this CO₂-free air standard gas
is twofold: one it has a known δ¹⁸O value and second as it has no interference from possible
CO₂ 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 δ(^34O/^32O) values obtained by parallel measurements using our IRMS.

Figure 18 shows the δ^{18}O values of ambient air from the roof top with three consecutive measurements of glass flasks filled with CO\textsubscript{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\textsubscript{2} in addition to O\textsubscript{2}, which can possibly interfere with the CRDS analyzer measurements, we have removed H\textsubscript{2}O and CO\textsubscript{2} by using a cryogenic trap (-130 °C) and in an additional experiment using Schütze reagent to remove both CO and CO\textsubscript{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\textsuperscript{-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\textsubscript{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 O₂ values during the presence of high CO₂ 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 CO₂ 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.

**Acknowledgement**

We would like to thank ICOS-RI and the Swiss National Science Foundation (SNF) for funding ICOS-CH (20FI21_148994, 20FI21_148992). We are also grateful to the International Foundation High Alpine Research Stations Jungfraujoch and Gornergrat. The measurement system at the Beromünster tower was built and maintained by the CarboCount-CH (CRSI2_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). Measurements are on the Bern scale for CO₂ and O₂. The Bern scale is shifted by +550 per meg. Values 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>CO₂-NDIR (ppm)</th>
<th>O₂-IRMS (per meg)</th>
<th>O₂-Paramagnetic (per meg)</th>
<th>O₂-CRDS (per meg)</th>
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</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>
<td>-1057</td>
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<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>
<td>590</td>
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<tr>
<td>ST-3 CA07045-Scripps</td>
<td>382.303</td>
<td>-271.6</td>
<td>382.50</td>
<td>381.99</td>
<td>278 (-272.2)³</td>
<td>302</td>
<td>281</td>
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<tr>
<td>ST-4 CA07043-Scripps</td>
<td>390.528</td>
<td>-476.4</td>
<td>390.69</td>
<td>390.15</td>
<td>71 (-479.5)³</td>
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<td>63</td>
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<tr>
<td>ST-5 CA07047-Scripps</td>
<td>374.480</td>
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<td>374.70</td>
<td>374.17</td>
<td>-253 (-803.3)³</td>
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<td>-233</td>
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<td>ST-6 CA04556-NOAA</td>
<td>192.44</td>
<td>-3410</td>
<td>191.21</td>
<td>191.64</td>
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<td>-2905</td>
<td>-3013</td>
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<td>ST-7 CA06943-NOAA</td>
<td>2699.45</td>
<td>-</td>
<td>2612.80</td>
<td>-</td>
<td>-2691</td>
<td>-3369</td>
<td></td>
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<tr>
<td>ST-8 LK76852-UB</td>
<td>411.49</td>
<td>37794</td>
<td>411.49</td>
<td>406.25</td>
<td>37794</td>
<td>34513</td>
<td>36017</td>
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</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 (m)</th>
<th>Oxidation Ratios (O$_2$:CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>-0.98 ± 0.06 (0.48)</td>
</tr>
<tr>
<td>44.6</td>
<td>-1.29 ± 0.07 (0.50)</td>
</tr>
<tr>
<td>71.5</td>
<td>-1.49 ± 0.08 (0.47)</td>
</tr>
<tr>
<td>131.6</td>
<td>-1.23 ± 0.05 (0.55)</td>
</tr>
<tr>
<td>212.5</td>
<td>-1.60 ± 0.07 (0.61)</td>
</tr>
</tbody>
</table>

List of Figures
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 $y = 1.417 - 0.023 x_{O_2}$ and $z = 0.481 + 0.085 x_{O_2}$.
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: $y = 1.4109 + 0.467 f_{\text{H}_2\text{O}}$. 
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 $\delta(^{18}\text{O})$ 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).
Figure 13. Parallel ambient air measurements by the Paramagnetic and CRDS analyzers at the beginning of the testing period (Panels a & b, January 2017) and the second phase of testing (Panels c & d, September 2017). The spikes are measurements from the two standard gases bracketing the ambient air values.
Figure 14. Parallel water vapor measurements for a dried ambient air by both the NDIR and CRDS analyzers. Note that the water values from the NDIR analyzer are not calibrated.
Figure 15. Results of water correction tests. Water measurements of the NDIR (left scale) for dry conditions (a,b) and the CRDS analyzer (right scale) for dry (a) and wet (b) conditions. The difference in oxygen measurements between the Paramagnetic and the CRDS instrument using the built-in water correction for the CRDS values under dry (c) and wet (d) conditions. Panels (e) and (f) show the population density functions.
Figure 16. Calibrated ambient air oxygen measurements (1-minute average) at the Jungfraujoch site using the CRDS and Paramagnetic analyzers both in ppm units (a) and the absolute difference between the two measurements in ppm (b) by matching time stamps.
Figure 17. Diurnal variations of CO$_2$ (top) and O$_2$ (bottom) measurements from the 12 m (red) and the 212.5 m (black) height levels at Beromünster tower.
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.
Appendix A.

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.
Appendix B: Uncertainty consideration during conversion of ppm to per meg

Generally, the Delta notation (δ(O₂/N₂)), as given in equation 1 of this publication (also shown below), is used in order to circumvent the influences of dilution by other gas components when determining oxygen mole fractions. Yet, several instruments are measuring the oxygen mole fraction such as the paramagnetic cell, the UV-cell as well as the instrument by CRDS analyzer presented here. Therefore, a thorough consideration of the conversion from ppm (mole fraction) to per meg (δ(O₂/N₂) notation) is necessary which is explained in this appendix.

Following equation 1 in Thojima et al., 2000, the per meg to ppm conversion has a slope of 6.04 if only a change in oxygen is applied as seen in table A1. It changes slightly to 6.11 per meg per ppm, when we talk about nitrogen changes only, or to a slope zero (horizontal line) when talking about any other changes of air components excluding oxygen and nitrogen. The fact that our supplementary plot shows slopes of 5.78 (for the first five standards) or 6.08 (for all standards except ST-7) is due to a mixed influence dilution effects. The lower slope of 5.78 documents particularly the influence of the CO₂ dilution effect.

\[
\delta (\frac{O_2}{N_2}) \text{(per meg)} = \left( \frac{O_2_{\text{sample}}}{N_2_{\text{reference}}} - \frac{O_2_{\text{reference}}}{N_2_{\text{reference}}} \right) \times 10^6 \quad (1)
\]

Note that under the assumption the atmospheric N₂ content is constant (i.e. N₂sample equals N₂reference), we convert relative changes in oxygen given in per meg following equation 1 to oxygen changes in parts per million (equivalent to micromol/mol) by multiplying by the O₂ mole fraction (O₂reference) expressed as 209500 ppm (the O₂ mole fraction of atmospheric air) (Macht and Hughes, 1970). Hence 1 ppm corresponds approximately to 4.8 per meg, or 1 per meg to 1/4.8 (209500/106) ppm.
This is used in our approach since the Picarro instrument measures the $O_2$ concentration which requires to be converted to an $O_2/N_2$ ratio. Since no information about $N_2$ is available one assumes a constant value, i.e. $N_2$ of the standard. Therefore, eq. 1 in the manuscript reduces to $(O_{2,SA}/O_{2,ST}-1) \times 10^6$ or $\Delta O_2/O_{2,ST} \times 10^6$. The value obtained is an estimated $\delta O_2/N_{2,est}$ ratio, which indeed is slightly different from the true $\delta O_2/N_{2,true}$. The effect of water dilution (amount of water vapor is measured by the CRDS instrument) is taken into account as described in the manuscript. Yet any other dilution effect is not considered except if additional information is available, e.g. $CO_2$ concentration measurements. Indeed this dilution effects can be significant and are displayed in the following table A1.

Table A1: ppm to per meg conversion calculations for air-like compositions

<table>
<thead>
<tr>
<th>Change in ppm</th>
<th>$\Delta O_2$ apparent (change + dilution effect)</th>
<th>$\delta O_2/N_{2,true}$ (per meg) ($\delta O_2/N_{2,true}/\Delta O_2$ in per meg/ppm)</th>
<th>$\delta O_2/N_{2,est}$ (per meg) ($\delta O_2/O_{2,est}/\Delta O_2$ in per meg/ppm)</th>
<th>Difference in $\delta O_2/N_2$ (true – est) in per meg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta CO_2$ only</td>
<td>10 -2.0946</td>
<td>0 (0)</td>
<td>-10 (4.77)</td>
<td>10</td>
</tr>
<tr>
<td>$\Delta Ar$ only</td>
<td>10 -2.0946</td>
<td>0 (0)</td>
<td>-10 (4.77)</td>
<td>10</td>
</tr>
<tr>
<td>$\Delta O_2$ only</td>
<td>10 7.9054</td>
<td>47.74 (6.04)</td>
<td>37.74 (4.77)</td>
<td>10</td>
</tr>
<tr>
<td>$\Delta O_2$ only</td>
<td>10 -2.0946</td>
<td>-12.81 (6.11)</td>
<td>-10 (4.77)</td>
<td>-2.81</td>
</tr>
</tbody>
</table>

$\delta O_2/N_{2,true}$: for instance measured by mass spectrometry; $\delta O_2/N_{2,est}$: for instance measured by Picarro G-2207.

Incorrectly assumed $N_2$, Ar, $CO_2$ or any additional gas component can lead to changes in the estimated $\delta O_2/N_{2,est}$ values as stated in the table A1. For example a 10 ppm increase in $CO_2$ lead to an incorrect value of -10 per meg in $\delta O_2/N_{2,est}$ compared to the true $\delta O_2/N_{2,true}$ value.
This is simply the dilution effect that the increased CO\(_2\) concentration has on the corresponding O\(_2\) concentration measurements (dilution in oxygen corresponds to the percentage-wise assignment of the excess CO\(_2\) in ppm to oxygen, i.e. \(-10\) ppm x oxygen mole fraction = 2.0946, if O\(_2\) mole fraction corresponds to 0.20946). As you can see from table A1, an addition of N\(_2\) of 10 ppm leads to a reduced and opposite effect for the difference in \(\delta\)O\(_2\)/N\(_2\) (true – est) because the dilution effect on O\(_2\) cannot compensate the change from the increase in nitrogen, therefore it scales with \(-10\) ppm x (oxygen mole fraction/nitrogen mole fraction). This also shows that the difference in the Delta values (true – est) scales with the \(\delta\)O\(_2\)/N\(_2\) ratio present in the sample. Therefore, best results are obtained when the calibration gases for which the gas composition is known equals closely the sample gas composition. In our case this is given – but can certainly be improved – since we are comparing air composition to air standard compositions. Yet, determinations of the standards that has been used in this study have a range in N\(_2\) concentrations of -110 to +110 ppm for the ST-1 to ST-5, whereas ST-6 (+700 ppm) and ST-8 (-6200 ppm) are significantly off compared to our primary standard used for mass spectrometric determination. Therefore, special attention is required for the precise determination of standard gas composition and the control of the air sample composition by means of flask measurements in order to detect potential fractionation effects during air intake.
References


Manning, A.: Temporal variability of atmospheric oxygen from both continuous and measurements and a flask sampling network: tools for studying the global carbon cycle, Ph.D., University of California, San Diego, San Diego, California, USA, 2001.


