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Evaluation of a cavity ring-down spectrometer for in situ observations of $^{13}CO_2$

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Abstract. With the emergence of wide-spread application of new optical techniques to monitor $\delta^{13}C$ in atmospheric CO_2 there is a growing need to ensure well-calibrated measurements. We characterized one commonly available instrument, a cavity ring-down spectrometer (CRDS) system used for continuous in situ monitoring of atmospheric $^{13}CO_2$. We found no dependency of $\delta^{13}C$ on the CO_2 concentration in the range of 303–437 ppm. We designed a calibration scheme according to the diagnosed instrumental drifts and established a quality assurance protocol. We find that the repeatability (1-σ) of measurements is 0.25 ‰ for 10 min and 0.15 ‰ for 20 min integrated averages, respectively. Due to a spectral overlap, our instrument displays a cross-sensitivity to CH_4 of 0.42 ± 0.024 ‰ ppm^{-1}. Our ongoing target measurements yield standard deviations of $\delta^{13}C$ from 0.22 ‰ to 0.28 ‰ for 10 min averages. We furthermore estimate the reproducibility of our system for ambient air samples from weekly measurements of a long-term target gas to be 0.18 ‰. We find only a minuscule offset of 0.002 ± 0.025 ‰ between the CRDS and Environment Canada's isotope ratio mass spectrometer (IRMS) results for four target gases used over the course of one year.

1 Introduction

The importance of the carbon cycle in the Earth system cannot be overrated as all living organisms participate and rely on it directly or indirectly. Besides understanding the biogenic components of the carbon cycle and its response to future changes in climate, the anthropogenic alterations of the carbon cycle, most prominently observed in the increase in atmospheric CO_2 and the acidification of the oceans, have been moving into the forefront of the atmospheric research community (Solomon et al., 2007). Studies aimed at distinguishing different sources of atmospheric CO_2 and investigating the underlying processes have frequently included carbon isotope analysis. Carbon-13 (^{13}C), the stable isotope of carbon for example, has been used in numerous studies to infer isotopic discrimination by plants during photosynthesis and isotopic composition of soil and plant respiration (e.g. Yakir and Wang, 1996; Ekblad and Högberg, 2001; Pataki et al., 2003). The information gathered from ^{13}C observation has also been used to quantify anthropogenic emissions of CO_2 (e.g. Zondervan and Meijer, 1996; Bakwin et al., 1998; Zimnoch et al., 2004; Pataki et al., 2006). Previous studies mostly relied on discrete grab sample measurements and thus provide only limited temporal resolution. Flask sampling also tends to be costly for high resolution measurements. With the emergence and improvement in optical spectrometers (e.g. cavity ring-down spectroscopy), affordable and reliable technologies appear within reach to conduct studies with quasi-continuous temporal resolution. The aim of this paper is to assess the performance of one type of currently commercially available cavity ring-down spectrometer and to suggest a strategy to ensure well-calibrated measurements to come as close as possible to the WMO recommended target for data compatibility. We characterize the signal-to-noise ratio, the temporal drift and the cross-sensitivity of this instrument and develop a calibration scheme according to our findings. The performance of our system is evaluated with our quality assurance (QA) routines which include using two categories of target gases. The results are evaluated over the course of one year of measurements. Although our current systems cannot

fulfill the WMO recommendations in inter-laboratory comparability due to the limited signal-to-noise ratio, our calibration strategy could be applied for future CRDS instruments that will be closer to achieving this goal when the fundamental signal-to-noise ratio is further improved. Although our CRDS instrument is capable of measuring CO_2 and H_2O levels as well, this paper only addresses ^{13}C in CO_2.

2 Instrumental setup

The core of our setup consists of a commercially available cavity ring-down spectrometer (CRDS) (G1101-i+, Picarro, Santa Clara, USA). This instrument has a built-in wavelength monitor as well as pressure and temperature control systems to ensure high stability of these parameters. The effective path length of the cavity is up to 20 km. The cell has a volume of 35 mL and the pressure within the cell is kept at 140 torr (i.e. 187 hPa). The small cell volume is one of the advantages of this CRDS system as it needs only little amounts of calibration gas (i.e. 35 mL min^{-1}) compared to other in situ instruments that need flows of 400 mL min^{-1} to 1000 mL min^{-1} (cf. McAlexander et al., 2011; Tuzson et al., 2011; Hammer et al., 2012; Griffith et al., 2012). The consumption, however, is still not comparable to the minimal amounts needed for our classical IRMS systems (Huang et al., 2012), that allows to measure smaller samples. For our CRDS instrument the abundance of $^{13}CO_2$ and $^{12}CO_2$ are determined independently from two spectral lines in the near-infrared (near 6251 cm^{-1}) before calculating $\delta^{13}C$ (Zare et al., 2009). Although measuring wet gas streams is possible with this system, we follow the strategy of avoiding negative impacts rather than to correct for these afterwards. We also found that rapid water level changes can slightly affect the retrieved $\delta^{13}C$, when applying the correction.

In our setup (Fig. 1), an external mass flow controller (MFC) (Alicat Scientific, Tuczon, USA) delivers a constant sample flow of 35 mL min^{-1} to the system. Prior to entering the spectrometer, the sample gas is passed through a magnesium perchlorate cartridge (air volume, < 10 mL) to dry the sample gas to a dew point of −80 °C. This design ensures that both the gas standards and the ambient sample air have the same level of moisture. A gas selection valve (Valco instrument, Houston, USA) is used to select between the various sample gas streams. In order to minimize the frequency of changing the chemical dryer, the ambient air is pre-dried to −30 °C by first passing the ambient gas through a Peltier cooler (M&C TechGroup, Ratingen, Germany) located upstream of the selection valve. We determined that a flushing time of 3 min is sufficient to flush the sample cell and ensure no residual sample from the previous stream is left. This was evaluated using two cylinders with differences of isotopic composition of more than 30 ‰. If future instruments, with higher precision, become available this should be revisited, as measureable cross contaminations are known to
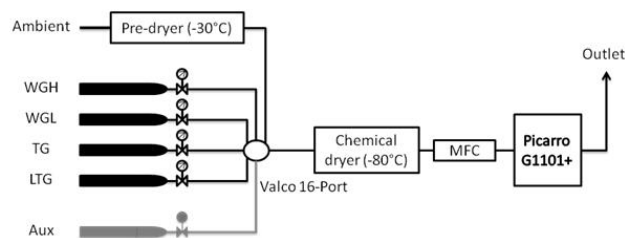
Fig. 1. Schematic setup of the in situ $^{13}CO_2$ monitoring system: the working gases high (WGH) and low (WGL) as well as the target gases (TG and LTG) and the pre-dried ambient air are connected to a rotary valve. After this all gases share the same path through a chemical dryer (Mg[ClO$_4$]$_2$) and an external mass-flow controller (MFC) before entering the cavity ring-down spectrometer.

cause scale contractions (e.g. Meijer et al., 2000; Gosh et al., 2005).

The inlet pressure for all sample lines ranges from 12 to 16 psi. The measurement sequence and valve control are done using the *valve sequencer* software provided by the manufacturer Picarro Inc. Santa Clara, USA.

3 Characterization of the instrument

3.1 Noise and stability

In order to characterize the noise and the drift behavior of the instrument, we used a cylinder with known $\delta^{13}C$ and monitored the changes of the instrumental output signal over time. For the 2-s high temporal resolution data, we found that the $\delta^{13}C$ data displays on average, a standard deviation of around 1.8 ‰ (cf. Fig. 2). The measurement noise is governed by the laser stability or noise. Furthermore, the rather weak absorption in the near-infrared, together with the quality of the optical cell limits the signal-to-noise ratio. Given the high precision needed to interpret $\delta^{13}C$ signals, we find that aggregating the raw data helps, as it, as expected, decreases the standard deviation. For 5 min averaging intervals, the standard deviation of 0.2 ‰ is actually better than the specification provided by the manufacturer for this system (i.e. 0.3 ‰). To achieve a precision level lower than 0.1 ‰, integration times of 60 min or more are required. We also determined that the WMO recommended precision value of 0.01 ‰ is not achievable using the current version of the CRDS instrument. However, for applications where strong variations of the $\delta^{13}C$ signal are expected, i.e. in urban measurements or terrestrial forested sites (high diurnal CO_2 signals), such high precision requirements might not be necessary. Given the limitations of the instrument, we have set our target for an accuracy level of 0.2 ‰, which at current CO_2 concentrations is equivalent to the addition of approximately 5 ppm of CO_2 from, for example, fossil fuel burning or respiration from biogenic sources. Given this goal, we have devised a sampling strategy by introducing measuring cycles
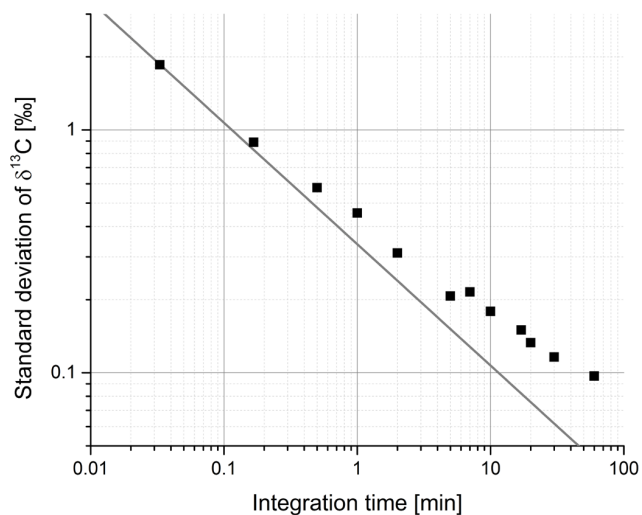
Fig. 2. Standard deviation for the measurements of CBDS-48 using constant flow from a single cylinder, using different integration times. The grey line gives the theoretical predication for random (white) noise.

Fig. 3. Instrumental drift of the Picarro $\delta^{13}C_{raw}$ monitored over 2 days using two gas cylinders TG48-A (black) and LTG48-A (red) measured twice per hour. To highlight the trend a running mean (6 h window) is given in the solid lines.

every 30 min, including target gases for 10 min and ambient air or calibration gases for 20 min, respectively. With a 3 min flushing time requirement between gases, this results in 17 min of valid data. Based on the single tank test experiment, as shown in Fig. 2, an average precision (repeatability) of 0.15 ‰ is achievable for 17 min intervals.

3.2 Long-term variations

Along with the short-term variations, the instrument also usually displays noticeable long-term drifts which can be as high as 1 ‰ over one day (Rella, 2012). Similar tests on our instrument as shown in Fig. 3, typically display less drift and show changes on the order of around 0.3 ‰ over the course of one day. We monitored the long-term behavior using two cylinders (LTG48-A and TG48-A) that were used to alternatingly flush the system for 10 and 20 min respectively, over several days. As shown in Fig. 3, we found that after subtracting the mean $\delta^{13}C$, both cylinders display similar drift patterns. Based on these long-term test results, we deduced that calibrating the instrument at least every 10 h and linearly interpolating the instrumental response between bracketing standards is more than sufficient to capture this behavior within 0.1 ‰. We decided to calibrate every 7 h as this ensures that the calibration does not systematically occur at the same time of day. To test the calibration frequency, we ran a QA routine to measure a target tank with a known $\delta^{13}C$ every 30 min. We found that monitoring this drift (or lack thereof after calibration) can be achieved using 10 min integrated averaging measurements (Fig. 3). This permits the lifetime of the target to last for more than 400 days ($\sim$ 7500 L) and provides frequent independent checks of the calibrations. The target gas can also be used to identify
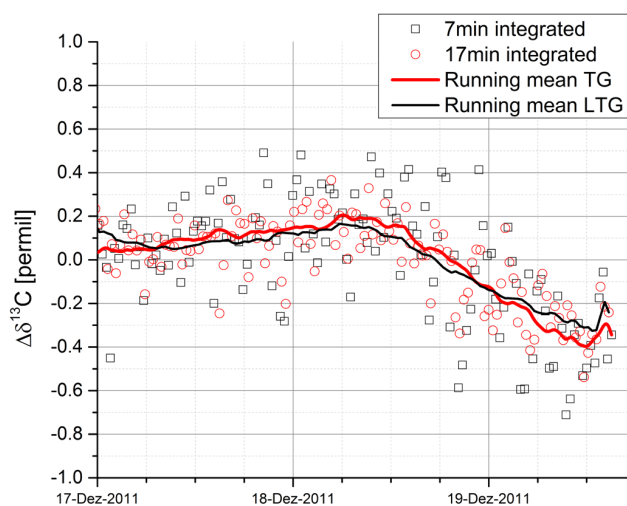
situations of unusual instrument behavior changes within the 7-h calibration interval. The choice of 10 min target measurements within a 30 min measurement cycle is usually a trade-off between capturing short-term drifts and maximising the time of ambient air observation. After the evaluation period of this instrument, presented in this paper, we changed the target measurement frequency to 10 min every 60 min. Other measurement programs should determine which trade-off is optimal for their purposes.

For this study, however, all our measurement cycles consist of 30 min, beginning with 10 min of a target gas followed by 20 min of another gas and a calibration every 7 h (cf. Fig. 4). In order to assess the performance of the ambient measurements and to monitor for longer-term drifts, we have introduced a second so-called "long-term" target (LTG) that is also measured for four subsequent measurements of 20 min once a week. To increase the precision for the long-term these measurements can then be averaged for each week. The lifetime of the long-term target is more than 50 yr ($\sim$ 7500 L cylinder), much longer than the expected lifetime of the instrument. This long-term target also helps to link the measurements over the lifetime of several working gases (WG) that are needed to determine the instrumental response and link our measurements to international scales. This is a vital component of the calibration strategy in ensuring long-term stability of the measurements and permitting back track corrections of the data due to scale changes or other reasons. The working gases, which link our raw data to the VPDBCO2-scale, are expected to last for more than 8 yr ($\sim$ 7500 L cylinder), as 0.7 L are consumed for each calibration, performed every 7 h.

Fig. 4. Measurement cycle of the CRDS system for target, ambient air, working gases and long-term target. Note that the first 3 min of each measurement is neglected to ensure an adequate flushing of the optical cell.

Fig. 5. Dilution experiment using two gas streams to vary the CO_2 concentration while maintaining a constant $\delta^{13}C$ to infer potential CO_2 concentration dependency.

3.3 Concentration dependence

Instruments are often deployed at measurement sites (Egbert, ON, CA and Toronto, ON, CA) that are both subject to strong anthropogenic and biospheric CO_2 fluxes where large ranges of isotopic compositions and CO_2 concentration will occur. To avoid systematic biases due to any CO_2 concentration dependency of the $\delta^{13}C$ observations, we conducted a series of dilution experiments over several days using a cylinder of known $\delta^{13}C$ and CO_2 concentrations. The air stream was split into two, with the first stream being completely stripped of CO_2 using two cartridges containing Ascarite II (Fisher Scientific, Hampton, USA). It is vital that this stream be void of CO_2 because the residual CO_2 from this stream could be highly fractionated. We separately analyzed the effluent from this stream and found the CO_2 concentration level to be well below our detection limit of less than 0.1 ppm. The second stream was unaltered. The two streams were merged in a static mixing chamber with the contribution from both streams being controlled using two manual needle valves (Swagelok, Solon, USA). All measurements where conducted over 3 days with each day starting off with the measurement of the unaltered gas stream ($[CO_2] = 437$ ppm, $\delta^{13}C = -11.035$ ‰, $[CH_4] = 1972$ ppb) followed by testing the other stream to evaluated the effectiveness of CO_2 scrubber. Upon ensuring the stability of the two gas streams, the ratio of flow between the two streams was altered and after allowing for settling effects, the $\delta^{13}C$ value was derived over the 20 min measurement interval. Our measurements span a CO_2 concentration range from about 303 ppm to 437 ppm. The results in Fig. 5 show the uncertainty of the $\delta^{13}C$ values derived from the different dilution steps and
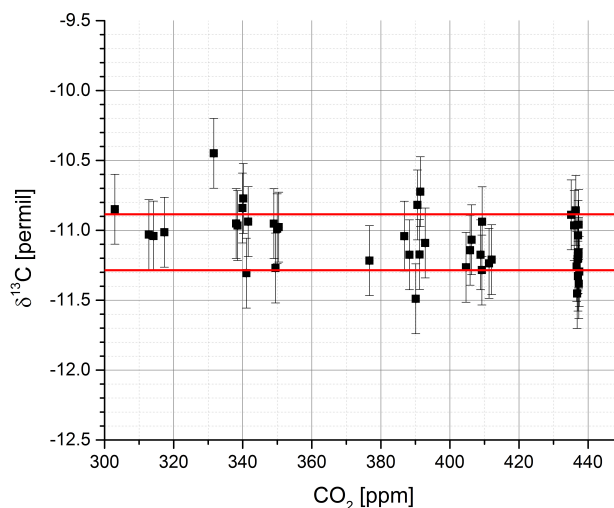
clearly demonstrates that there is no significant concentration dependency of $\delta^{13}C$ in this concentration range and that the standard deviation of our measurements to be around 0.2 ‰.

4 Calibration of raw data to the Vienna Pee Dee Belemnite scale

4.1 Scale offset and cross-sensitivity

In order to compare our results to other measurements such as data from the globally available flask networks and in situ data (http://ds.data.jma.go.jp/gmd/wdcgg/wdcgg.html), the data from our instrument must be calibrated on internationally recognized carbon isotope primary scales (the Vienna Pee Dee Belemnite (VPDB) scale). From our long-term experiments (cf. Sect. 3.2) we have determine that calibrating every 7 h is sufficient to capture drift patterns. Using multiple cylinders with known $\delta^{13}C$ values, which are all well anchored on the primary scale, i.e. VPDBCO$_2$ (Huang et al., 2012), we found that the raw Picarro scale is linearly dependent on the VPDB and has both a mean offset $b = 2.07$ ‰ and a slope of $m = 1.075$ ‰ ‰$^{-1}$ with inter-quartile ranges of 0.4 ‰ and 0.01 ‰ ‰$^{-1}$, respectively. It is apparent that the raw Picarro scale deviates significantly from the VPDBCO2 scale, well maintained at Environment Canada and it is indispensable to perform frequent online calibrations to retrieve $\delta^{13}C$ data in accordance (i.e. traceable) to VPDBCO2. We therefore measure two working gases with high (WGH) and low (WGL) $\delta^{13}C$ values to determine the current instrument response. To reduce the uncertainty of the fit a large isotopic range, i.e. -8 ‰ to -32 ‰, for the two working gases was chosen. And the (preliminary) $\delta^{13}C_{VPDB}$ value can be derived from our raw data using:

$$\delta_i^{13}C_{VPDB*} = \delta_i^{13}C_{raw} \cdot m + b. \qquad (1)$$

After applying this equation we found a residual difference between the calibrated and true $\delta^{13}C$ values, which was identified to be due to a cross-sensitivity of the instrument to the CH_4 mixing ratio of the sample. This cross-sensitivity is caused by an overlap of the absorption lines of CH_4 and $^{13}CO_2$. This complicates calibrating the instrumental signal (i.e. $\delta^{13}C_{raw}$), which consists of the response due to the ^{13}C levels ($\delta^{13}C_{res}$) and a CH_4 concentration ([CH_4]) dependent term scaled by a cross-sensitivity factor (X_{sens}).

$$\delta_i^{13}C_{VPDB*} = (\delta_i^{13}C_{res} + [CH_4]_i \cdot X_{sens}) \cdot m + b \qquad (2)$$

X_{sens} has been found to be both dependent on the H_2O as well as the CO_2 concentration (A. van Pelt, Picarro Inc. Santa Clara, USA, personal communication, 2012; van Pelt, 2012). For our application these effects can, however be neglected as all samples are dried (to the same level of moisture) and the dependence on the CO_2 concentration seems not to be significant and was not visible in our experiments (cf. Sect. 3.2). The calibrated and cross-sensitivity corrected $\delta^{13}C_{VPDB}$ can thus be derived from

$$\delta_i^{13}C_{VPDB} = \delta_i^{13}C_{res} \cdot m + b$$
$$= \delta_i^{13}C_{VPDB*} - [CH_4]_i \cdot X_{sens} \cdot m. \qquad (3)$$

To determine X_{sens}, one can use a set of at least three cylinders (A, B, C) with known $\delta^{13}C_{VPDB}$ and known CH_4 concentration to derive the cross-sensitivity from a linear regression. Following the equation:

$$X_{sens} = -\frac{\left(\delta_c^{13}C_{VPDB} - \delta_c^{13}C_{VPDB*}\right) \cdot \Delta_{A-B}\delta^{13}C_{raw}}{[CH_4]_c \cdot \Delta_{A-B}\delta^{13}C_{VPDB*}} \qquad (4)$$

using the convention $\Delta_{i-j}Q = Q_i - Q_j$.

The derived cross-sensitivity shows a large standard deviation (0.29 ‰ ppm^{-1}) as the signal-to-noise ratio for the individual terms in the equation is very poor. However, if we combine a large set of over 150 measurements we find that the cross-sensitivity did not show any temporal trends over several months with a mean of 0.42 ‰ ppm^{-1} and a standard error of ± 0.024 ‰ ppm^{-1}. Therefore, a sample with a typical concentration of 2 ppm has to be corrected by 0.84 ‰ with an uncertainty of 0.048 ‰ of this correction. Any potential bias introduced by this correction would be the same for both calibration gases as well as samples. The post-processing correction is done using the concurrent ambient measurements of CH_4 from our in situ gas chromatographic system (Worthy, 2003).

4.2 Data processing procedures

The high resolution 2-s raw data is at first averaged over 1-min interval to reduce storage space requirements. Using a MySQL compatible relational database system (MariaDB), the data is further averaged to 10 min intervals for the
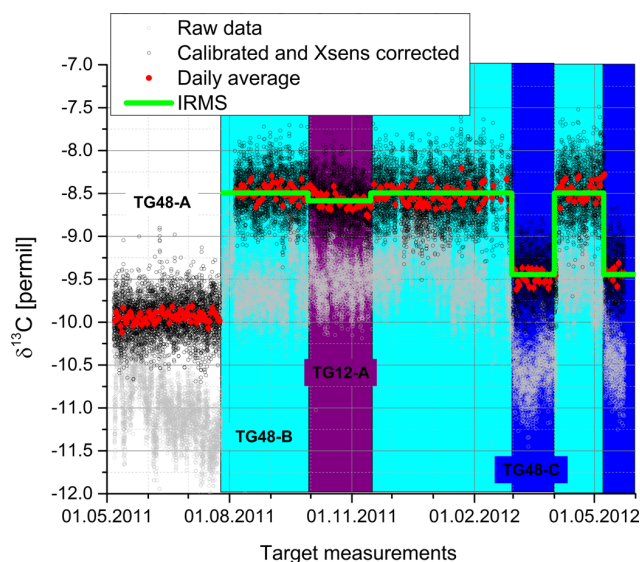
Fig. 6. Time series of the 10 min averaged target measurements passed through the system every 30 min. The Picarro raw data is shown in grey. The calibrated data is in black and daily averages of the $\delta^{13}C_{TG}$ are shown in red. The externally calibrated $\delta^{13}C$ values (using the EC IRMS system) are shown in green. Periods in which different sets of target gases are used are indicated by the background coloring (cf. Table 1).

target measurements and to 20 min intervals for the ambient air, calibration, long-term target and auxiliary measurements. Each sample switching triggers a flag that invalidates the first 3 min of each to ensure that the cell has been adequately flushed with the new sample. Therefore, abrupt strong changes in $\delta^{13}C$ might not be capture on a minute time-scale. The data is then calibrated using the instrument response according to Eq. (3), determined from the bracketing working gas measurements. After this the data is then flagged according to deviation of the target measurements from the true value that must be less than 0.75 ‰ and/or 0.15 ppm for the CO_2 mixing ratio. The data further flagged if water levels exceed 0.01 % in the sample and if the standard deviation of the ambient CH_4 and CO_2 mixing ratios of the averaging interval are above 0.1 ppm or 5 ppm, respectively. This pre-selected data is eventually visually inspected before being ultimately assigned as valid data and used in hourly and longer averaging time steps.

5 Quality assurance and control

5.1 Long-term stability of the target

The long-term stability of the frequent target measurements can be used to assess the long-term performance of the instrument as well as the adequacy of our calibration strategy to capture the changing instrument response and the CH_4 cross-sensitivity. Over the first year of measurements,

Table 1. Comparison of CRDS and IRMS values of target gas measurements. The standard error for the target measurements of the CRDS ($\delta^{13}C_{cal}$) are all below 0.01 ‰, yet the uncertainty is given as (< 0.1 ‰) as other sources of error have to be included (see text and cf. Fig. 6).

	CRDS					IRMS
Target ID	$\delta^{13}C_{raw}$	$\delta^{13}C_{cal}$ (uncertainty)	$\delta^{13}C_{cal}$ std.dev.	N	Working gas range	$\delta^{13}C_{MS}$ (uncertainty)
TG48-A	-10.96 ‰	-9.94 (< 0.1) ‰	0.22 ‰	> 5400	-32 ‰ to -8 ‰	N/A
TG48-B	-9.62 ‰	-8.47 (< 0.1) ‰	0.23 ‰	> 2600	-32 ‰ to -8 ‰	-8.495 (± 0.02) ‰
TG12-A	-9.51 ‰	-8.58 (< 0.1) ‰	0.23 ‰	> 2200	-24 ‰ to -9 ‰	-8.585 (± 0.02) ‰
TG48-B	-9.39 ‰	-8.52 (< 0.1) ‰	0.26 ‰	> 5000	-32 ‰ to -8 ‰	-8.495 (± 0.02) ‰
TG48-C	-10.56 ‰	-9.48 (< 0.1) ‰	0.26 ‰	> 1500	-32 ‰ to -8 ‰	-9.445 (± 0.02) ‰
TG48-B	-9.55 ‰	-8.47 (< 0.1) ‰	0.28 ‰	> 1500	-32 ‰ to -8 ‰	-8.495 (± 0.02) ‰
TG48-C	-10.49 ‰	-9.43 (< 0.1) ‰	0.27 ‰	> 900	-32 ‰ to -8 ‰	-9.445 (± 0.02) ‰

four different target gas cylinders have been used (TG48-A, TG48-B, TG48-C and TG12-A), over various periods (cf. Table 1). The 29 L aluminum cylinders (Scott Marin, Riverside, USA) were filled with dried ambient air using an oil-free Rix compressor (RIX Industries, Benicia, USA). After one year of measurements, we can see in Fig. 6 that the original instrumental output $\delta^{13}C_{raw}$ (in grey) shows significant long-term drifts. This is particularly pronounced in the first episode. We also find that there is a general offset between the "true" and the raw data. After calibrating the data and correcting for the CH_4 cross-sensitivity, we find that the 10 min averaged $\delta^{13}C$ target values still display a high standard deviation of around 0.25 ‰ but are stable over long periods with a standard error of below 0.01 ‰ for all episodes. The uncertainty estimate in table 1 of 0.1 ‰ includes the uncertainty of the X_{sens} and the uncertainty in the assigned values of the working gases.

The daily averaged target data nicely overlaps with the $\delta^{13}C$ that were determined using Environment Canada's IRMS system (Huang et al., 2012). In the third period (purple) a different set of working gases WGH12-A and WGL12-A was used spanning -9 ‰ to -24 ‰, as the calibration standards. For all other episodes WGH48-A and WGL48-A were used and spanned a range from -8 ‰ to -32 ‰. We found that our approach provides consistent results over the four different target gases used and is independent of which set of working gases was used. The standard deviation of target measurement ranges from 0.22 ‰ to 0.28 ‰ for all periods and the mean offset between the calibrated CRDS results compared to the IRMS data is 0.002 ‰ and with a standard deviation of 0.025 ‰. This implies that, although a single measurement can be quite imprecise, the CRDS system can provide accurate results if proper calibration procedures are applied.

5.2 Reproducibility and uncertainty estimation for ambient measurements

To assess the reproducibility of our ambient air measurements, we analyzed the measurements of the long-term target. The long-term target is measured once a week (cf. Fig. 4)
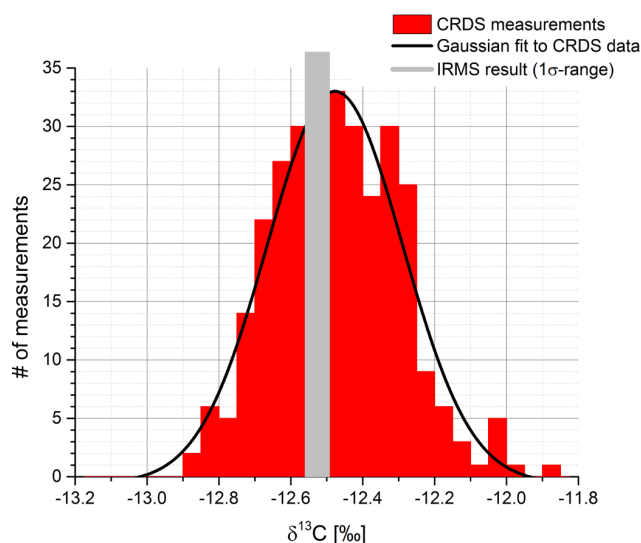
Fig. 7. Histogram of long-term target (LTG-48A) values between November 2011 and May 2012 from (four consecutive) measurements once per week in red and the IRMS value for LTG-48A in grey.

and is treated in the same manner as an ambient sample (in the measurement routine as well as during data processing). For the measurements included in this study (11 November– 12 May) a mean of -12.47 ‰ was determined. This compares well with the independently IRMS calibrated value of $\delta^{13}C$ -12.54 ± 0.03 ‰. The standard deviation (reproducibility) of the long-term target measurements is 0.18 ‰ and follows a distinct Gaussian distribution as shown in Fig. 7. This result is well in line with the expected standard deviation of 0.16 ‰ when including the 0.15 ‰ uncertainty due to the instrumental noise (cf. Sect. 3.1.), 0.02 ‰ uncertainty of the $\delta^{13}C$ of the calibration cylinders and 0.048 ‰ uncertainty of the CH_4 cross-sensitivity correction (cf. Sect. 4.1). Even when including all internal sources of error, our system is capable of providing long-term in situ observations of $\delta^{13}C$ in atmospheric CO_2 better than 0.18 ‰ for 20 min average values.

6 Discussion and outlook

We characterized a cavity ring-down spectrometer system used for continuous in situ monitoring of ^{13}C in atmospheric CO_2. We found no dependency of δ^{13}C on the CO_2 concentration within the range of 303–437 ppm and determined a cross sensitive to CH_4 of 0.42 ± 0.024 ‰ ppm^{-1}. We designed a calibration scheme according to the found instrumental drifts and established a QA protocol. We find that the repeatability of 10 min measurements is 0.25 ‰ and 0.15 ‰ for 20 min integrated averages over the course of one year. We determine the reproducibility of the system for ambient air measurements from weekly measurements of a long-term target gas to be 0.18 ‰. This is consistent with the theoretical prediction. We find that the uncertainty is dominated by the instrumental noise of 0.15 ‰ and less by the uncertainty of the calibration and the cross-sensitivity. Analyzing our target measurement performed for QA reasons, we find a negligible offset of 0.002 ± 0.025 ‰ between the results by our CRDS and the results by Environment Canada's IRMS, which is firmly anchored at the VPDB scale (Huang et al., 2012). Our calibration strategy is suited for this instrument. Our approach was already developed bearing in mind that future instruments will show better signal-to-noise characteristics and a thorough cross-sensitivity correction might be even more important. Recently developed instruments ("Data Sheet G2131-i", 17 July, available at: http://www.picarro.com/isotope_analyzers/co2_ambient) are reported to having a three-fold improved fundamental signal-to-noise ratio, which theoretically would allow for an accuracy of below 0.1 ‰ for 15 min integrals (at a flow of 0.035 L min^{-1}) using this calibration. Assuming that the cross-sensitivity can be determined with a higher precision, even measurements with accuracy of the order of 0.05 ‰ is in reach.

Other instruments used for in situ $^{13}CO_2$ observations are reported to have comparable or sometimes higher precision.

Tuzson et al. (2011) used a secondary standard gas to determine the long-term precision of their quantum cascade laser-based absorption spectrometer (QCLAS). For 2 min averages (at a flow of 0.4 L min^{-1}) they report it to be better than 0.2 ‰. For an off-axis integrated cavity output spectroscopy (ICOS) instrument, McAlexander et al. (2011) report a long-term precision of 0.11 ‰ for 35 min integrals (at a flow of 0.5 L min^{-1}). A detailed description and thorough calibration strategy for a Fourier-transform infrared spectroscopy (FTIR) instrument was given by Griffith et al. (2012) and Hammer et al. (2012). They found a total uncertainty (1-σ) for a single measurement of 0.07 ‰ using a 2.5 min integration time (at a flow of 1 L min^{-1}) and 0.03 ‰ for the reproducibility of their target gas measurements. It seems hard to predict which technology will be used for certain applications as besides the mere reproducibility other factors such as sample/standard gas consumption as well as robustness and handling will play a significant role.

Our approach presented in this study is applicable to CRDS systems as well as to other spectrometers and comprises the following steps: (i) Quantify the fundamental signal-to-noise ratio. (ii) Determine short-term and long-term drift of the instrument responses by measuring cylinders with known δ^{13}C values. (iii) Determine the calibration frequency needed to ensure the needed precision for the planned measurements. (iv) Identify external drivers and cross-sensitivities to other species (e.g. CH_4) and check for any concentration dependencies. (v) Establish a link of the instrumental scale to internationally recognized standards. (vi) Most importantly, a thorough QA routine using at least two target cylinders should be implemented. The value of frequent target gas measurements to monitor the instrumental drift on short time scales to identify erroneous situations and to flag bad data, in addition to a long-term monitoring scheme to determine the reproducibility of the system, as well as checking for any drifts in the scale established through the working gas cylinders, cannot be overestimated.

Copyright statement

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