

February 19, 2021

Response to reviewer comments for manuscript "Simultaneous measurement of $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$ of atmospheric CO_2 - Performance assessment of a dual-laser absorption spectrometer

We want to thank the reviewer for the constructive comments for the final version of our paper. In this document we will address the points raised by the reviewer. We use **bold text** for repeating the points of the reviewer, normal text for our answers, and *italics text* for changes made in the manuscript. Page and rule numbers apply to the new version of the manuscript.

1. **The abstract of the paper ends with the sentence, which is only partially supported by the main text. Authors might want to elaborate improvements in measurement procedure, spec. fit and $17O$ calibration.** We agree that the last sentence of the abstract is not supported by the text. We therefore removed the last sentence of the abstract. In the most recent version of the paper we included a more robust calibration of the $\delta^{17}O$ measurements by using assigned values, which were directly and indirectly derived from measurements at the IMAU. Also, due to adjustments that were made for the IM calibration method, precisions of the $\delta^{17}O$ improved significantly and are now closer to the required precision over the whole measurement period.

p.26 line 565: "These precisions are now not yet achieved, but the results of the IM calibrated values show that small improvements in the measurement precision of the SICAS can bring the $\Delta^{17}O$ measurements close to the 0.01 precision. This could for instance be accomplished by deciding to conduct more iterations per measurement, if sample size allows this. In section 2.2 the contamination of the mirrors was discussed as the potential cause for the decreased signal-to-noise ratio in over the period September 2017-July 2019. Placing new mirrors in the optical cell might therefore improve the quality of the measurements further. As the quality of the $\Delta^{17}O$ measurements depends directly on the quality of the $\delta^{18}O$ and the $\delta^{17}O$ measurements, it will be important to monitor the measurement quality of both isotope values over time using the measurements of the quality control gas. If SICAS measurements are to be used for comparison with $\Delta^{17}O$ measurements from other labs or measurement devices, it is necessary to add the error introduced by the scale uncertainties of the reference gases as well.

For both the $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ these uncertainties are 0.08, as calculated with a Monte-Carlo simulation as described in section 4.2. As long as only measurements from this device are used, seasonal and diurnal cycles are measured with much lower uncertainties. The high residuals found for the quality control gas measurements of the $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ show that these uncertainties are probably an underestimation, as the assigned values of the low and high reference, which were not directly measured at the IMAU, are not known with high accuracy. For reducing the combined uncertainty it is therefore crucial to have all reference gases directly determined for their $\delta^{17}\text{O}$ values, as well as reducing the scale uncertainties of both the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of the reference tanks. ”

2. **In recent years, significant progress has been made towards high-precision optical measurements of rare 17O-CO2 isotopologue:** doi.org/10.1021/acs.analchem.7b03582, doi.org/10.1021/acs.analchem.7b02853, doi.org/10.1021/acs.analchem.9b03316. **An overview of these works could be mentioned in the introduction.**
p. 3 line 65: ”Recent studies already showed the effectiveness of optical spectroscopy for the measurement of $\delta^{17}\text{O}$ in pure CO_2 for various applications (Sakai et al., 2017; Stoltmann et al., 2017; Prokhorov et al., 2019).”
3. (a) **a) what was the output power of ICLs?**
 (b) **were measurements realised in static or flow-through mode?**
Measurements were realised in static mode. p. 4, line 99: ”The gas inlet system, depicted in figure 3, is designed to measure discrete air samples in static mode, such that one can quickly switch between measurements of different samples. ”
 (c) **CO2 is known to be absorbed by aluminium, did authors encounter losses of gas in the optical cell?** We are aware of this characteristic of the cell, and loss of CO_2 is observed when letting a CO_2 -in-air mixture into the cell, after the cell was flushed with a CO_2 -free flush gas (in this case N_2). We did, however, conclude that these effects are negligible for measurements conducted in the atmospheric range. If samples of strongly deviating CO_2 mole fractions or isotope compositions are measured, scale contraction might occur. We believe, as this paper investigates the potential to measure atmospheric samples, investigations of this effect is outside of the scope of the paper. An extra sentence has

been added to the manuscript text regarding the surface adsorption effects. *page 9 line 174: If samples of CO_2 concentrations outside the range of atmospheric samples are measured it will be essential to also take into account the surface adsorption effects of the aluminum cell (Leuenberger et al., 2015), an effect that was observed clearly when measuring atmospheric samples right after the cell was flushed with (CO_2 -free) N_2 gas.*

(d) **typical level of residuals, absorption line profiles, and spectroscopic line parameters are not mentioned in the text. Figure 2 might be improved by adding subplots with fit residuals and reporting noise level.** Noise levels of the four relevant isotopologues are shown in figure 4 (upper panels). Figure 2 is adjusted and now also includes the residuals of the fits.

4. **The authors tested the novel calibration scheme based on the isotopologue mole fraction and compare it with a conventional isotope ratio calibration. Several groups demonstrated successful application of the isotopologue mole fraction calibration recently (doi.org/10.1088/1681-7575/ab948c and doi.org/10.1002/rcm.8836). Not too much effort has been made towards the explanation of the advantages and disadvantages of both methods. Discussion on spectroscopic principles and limiting factors of the methods fit the scope of the paper. The discussion given in the end of 4.1 is very brief. Authors might want to expand this section.** A general introduction before section 3.3.1 has been added to explain the main advantages/disadvantages of both calibration methods. *page 17, line 355: "Two different calibration strategies are discussed in this section. The calibration strategies are based on the two main approaches for calibration of isotope measurements, as also described by Griffith et al. (2012) and, more recently by Griffith (2018), being (1) determine the isotopologue ratios, and calibrate those, taking the introduced CMFD into account, from now on defined as the ratio method (RM), and (2) first calibrate the absolute isotopologue mole fractions individually and then calculate the isotopologue ratios, from now on defined as the isotopologue method (IM). We give a brief introduction of the two calibration methods, as described in literature and we describe the measurement procedure that is used for both calibration methods. This section ends with a detailed description of both methods as applied for the SICAS measurements. The RM, being very similar to calibration strategies applied by*

isotope measurements using DI-IRMS (Meijer, 2009), is usually based on reference gases covering delta values of a range which is similar to the range of the measured samples. Determination of the CMFD can be done by measuring different tanks of varying CO_2 mole fractions or by dynamical dilution of pure CO_2 with CO_2 free air (Braden-Behrens et al., 2017, Sturm et al., 2012, Griffith et al., 2012; McManus et al., 2015; Tuzson et al., 2008), again covering the CO_2 mole fraction range of the measured samples. The IM has the advantage that there is no need to take the introduced CMFD into account (Griffith, 2018). As all isotopologues are calibrated independently, it is only necessary to use reference gases covering the range of isotopologue abundances as occurring in the samples. This can be realised by using reference gases containing CO_2 of similar isotope composition but varying CO_2 mole fractions (Griffith et al., 2012; Griffith, 2018; Flores et al., 2017). The range of delta values that is measured in samples of atmospheric background air is limited (range in unpolluted troposphere is -9.5 to -7.5 en -2 to +2 for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively (Crotwell et al., 2020)), hence this also applies to the range of delta values that should be covered by the reference gases when applying the RM. We decided therefore to use the same reference gases to test both calibration methods, varying mainly in CO_2 mole fraction (342.81-424.52 $\mu\text{mol}/\text{mol}^{-1}$)."

Additional discussion on performances of both methods has been added to section 4.3. page 23 line 522: "To check the performance of the SICAS for both the IM and RM over the wide CO_2 range that is covered by the ICP sausage samples, the differences between the MPI-BGC and the SICAS results are plotted in figure 8 against the measured CO_2 mole fraction. Shown is that for both methods the highest differences are seen at the higher end of the CO_2 mole fraction above 425 ppm, and therefore far out of the range that is covered by the HR and LR cylinders (~ 343 -425 ppm). Extrapolation of the calibration methods outside the CO_2 mole fraction range of the reference cylinders yields worse compatibility with MPI-BGC, possibly due to the non-linear character of both the isotopologue CO_2 dependency and the ratio CO_2 dependency. It should therefore be concluded that, to achieve highly accurate results of isotope measurements over the whole range of CO_2 mole fractions found in atmospheric samples, the range covered by the reference cylinders would ideally be changed to 380-450 ppm. The results of the IM are slightly better in the CO_2 range above 425 ppm, specifically the point closest to 440 ppm shows a significantly smaller residual (~ 0.1 less) than the RM. The better result of extrapolation of the deter-

mined calibration curves for the IM method could be due to the lesser degree of non-linearity of the measured isotopologue abundances as a function of the assigned isotopologue abundances, in comparison to the non-linearity of the measured isotope ratios as a function of the CO₂ mole fraction. More points in this higher range are needed, however, to draw any further conclusions on this matter. ”

Also in section 4.4 additional discussion on performances of both methods has been added. *page 25 line 550: ”All results show too enriched values according to the assigned values, which is probably due to the fact that the assigned $\delta^{17}\text{O}$ values of the low and high references have been determined indirectly, as discussed in section 3.2. A direct determination of the $\delta^{17}\text{O}$ values of our low and high references would supposedly improve the accuracy of both methods. The $\Delta^{17}\text{O}$ accuracy is dependent on both the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ results, where $\Delta^{17}\text{O}$ values will deviate more if those results deviate in opposite directions and vice versa. Furthermore, it is striking that the mean standard errors of measurement periods 2 and 3 are twice as low for the IM than for the RM. The r^{627} , used for the RM, is calculated by dividing X_{627} , derived from laser 1, by X_{626} derived from laser 2. It can be that the two lasers do not drift in the same direction and the advantage of cancelling out these drifts by dividing the two measured values will not apply. The outlier analysis of the IM might in that case be more effective as it is performed on both the measured ^{16}O and ^{17}O abundances, while for the RM it is only performed on the r^{627} . A comparison of the correlation coefficients between the 627 peak results and the 626 peak results from both lasers shows no significant difference (and a value of ~ 0.65), meaning that using the 626 peak of laser 1 for the $\delta^{17}\text{O}$ calibration will not improve the precision of the RM results. ”*

5. **This paper might attract more readers if it ends with a crisp recommendation summary on how to operate the laser-based isotope ratio spectrometer in practice. The findings reported in the paper are sufficient for this.** We added all calculation steps for both calibration methods in the appendix. In addition, a section on the used measurement procedure was added to the text, so future users will have a better view on how to use this device in practice. *page 17 line 376:”The measurement procedure that is used for both calibration methods is based on the alternating measurements of samples/reference gases and the WG, so the drift corrected measurement value can be calculated as in equation 1. Per sample/reference gas measurement,*

there are 9 iterations of successive sample and WG measurements, from now on called a measurement series, before switching to the next sample/reference gas measurement series. One measurement series lasts ~ 30 minutes. Sample series are conducted once, while the reference gases series (LR and HR) are repeated 4 times throughout a measurement sequence. The QC, a gas of known isotope composition which is not included in the calibration procedure, is also measured 4 times throughout the measurement sequence. One measurement sequence in which 12 samples are measured lasts therefore ~ 12 hours. For the 9 measurement values of each measurement series outliers are determined using the outlier estimation method for very small samples by Rousseeuw and Verboven (2002), and the mean values of the measurement series are calculated. For a complete step-by-step guide of all calculation steps for both calibration methods, please see Appendix C"

6. The paper would benefit from reduced use of abbreviations.

I also suggest using roman typesetting for chemical formula and conventional (not AFGL) notation for isotopologues, e.g., $^{12}\text{C}^{16}\text{O}_2$ instead of 626. Captions of the figures and tables might be extended for Figs. 1 – 3, and Tabs. 1 – 4. The use of abbreviations has been reduced, for instance by not abbreviating the names of the reference cylinders anymore. We continue to use the HITRAN notation, as this is in our view an accepted notation in the field of spectroscopy and is much shorter. The captions of figures 1-3 have been extended, as well as for tables 1-4. Figure 1 has been changed to a more schematic view of the components on the SICAS optical bench for clarity.

7. Parts of the main text with technical details that are not directly related to the main subject of the paper, e.g., p.9 starting line 199, might be moved to the Appendix.

The following section has been moved to Appendix A: "The pure CO_2 aliquots were prepared by connecting a 20 mL flask containing a pure CO_2 local reference gas to a calibrated adjustable volume. The required amount of CO_2 in the adjustable volume could be determined by measuring the pressure at a resolution of 1 mBar using a pressure sensor (Keller LEO 2). Both the sample flask and adjustable volume were connected to a vacuum (3.3×10^{-5} mBar) glass line. The CO_2 in the adjustable volume was transferred cryogenically (using liquid nitrogen) into a small glass tube shape attachment on the side of the evacuated sample flask which was custom-made for this purpose and subsequently the zero-air dilutor gas was added. The dilutor gas consists of natural air scrubbed of

CO₂ and H₂O using Ascarite[®] (sodium hydroxide coated silica, Sigma-Aldrich) and Sicapent[®] (phosphoric anhydride, phosphorus(V) oxide), which results in dry, CO₂-free natural air. For experiment 2, additional samples were prepared using synthetic air mixtures with and without 1% Argon as dilutor gas for evaluation of the effect of air composition on the CMFD (see also section 3.1.6). After closing the flask, the mixture was put to rest for at least one night before measurement to ensure the CO₂ and the dilutor were completely mixed. ”

Some technical corrections:

page 2, line 40: isobaric interferences of $m/z = 46$ with $m/z = 45$?
Please elaborate What we mean to say here is that the $^{12}C^{17}O^{16}O$ has the same mass as $^{13}C^{17}O^{16}O$ and will interfere when doing IRMS measurements. Idem for the $^{13}C^{17}O^{16}O$ and $^{12}C^{17}O^{17}O$ with $^{12}C^{18}O^{16}O$. We do believe this is stated clearly and correctly and therefore no changes to the text are made.

page 3, line 80: citation to out-dated HITRAN version. This reference is updated to Gordon et al., 2017.

page 4, figure 1: label in the figure contradicts main text (QCL vs ICL). The label in the figure is adjusted.

page 4, figure 2: typical level of fit residuals might be added here. Fit residuals are added to the figure.

page 5, figure 3: not all elements of the diagram are explained. The caption of the figure is extended and a legend is added to the figure to explain all elements of the diagram.

page 9, line 201: here and throughout the text, mbar, not mBar or mBars Is adjusted as suggested.

page 9, line 291: cite doi.org/10.5194/amt-13-2797-2020 for matrix effect in mid-IR analysers This reference is added, and the text has been changed slightly. *page 15 line 308 in modified manuscript : It is known that for laser spectroscopy the composition of the sample air affects the absorption line profiles by pressure broadening effects (“matrix effects”), with non-negligible consequences (Nakamichi et al., 2006, Nara et al., 2012, Harris et al., 2020). Hence, it is likely that air composition affects CO₂ isotope measurements for the SICAS as well.*

page 15, line 311: purity $\leq 99.99\%$? *page 15, line 313 in modified manuscript changed to purity $\geq 99.99\%$*

page 16, table 5: briefly explain the errors Errors are now explained in the table caption.

page 17, line 364: cite doi.org/10.5194/amt-11-6189-2018 This reference has been added in section 3.3.

Sincerely,

Farilde Steur