

Interactive comment on “Simultaneous measurement of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of atmospheric CO_2 – Performance assessment of a dual-laser absorption spectrometer” by Pharahilda M. Steur et al.

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Received and published: 22 December 2020

General comments

Over recent years the introduction of optical systems based on various spectroscopic techniques has revolutionized stable isotope analysis in the atmosphere requiring a full calibration process with appropriate standards that are value assigned on internationally recognized scales, both for mole fraction and isotopic composition.

This paper proposes a new optical system and compares two calibration procedures.

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Regarding the information on the instrument this paper provides straightforward technically detailed description of a QCL laser-based analyzer. However, the text about the injection of the samples into the gas cell misses very basic information (static or dynamic flow (l/min?), type of materials, treatments, flushing and gas handling procedures (cylinder and flasks) for example).

Concerning the calibration procedures this paper presents important conclusions on methods (RM and IM), but these conclusions are based on results which miss robust uncertainty analysis. Most of the uncertainties considered in the paper are statistical (precision), without proper consideration if systematic uncertainties can be discarded (for example from calibration). Additionally, important changes in the experimental conditions, significant decrease of about 50 percent in the measured laser intensity, happened and it is not clear how it influenced the results measured during the period 2017-2019.

This paper may be suitable for publication in AMT only after major revisions are to increase its robustness.

Technical comments:

- 1) Page 3, line 89: Please provide details on the type of materials, treatments on lines and valves to transfer the gas to the SICAS instrument. Is the gas cell under constant gas flow? If yes please provides the flow rate.
- 2) Page 5, line 91: Describe in detail the flushing procedure to avoid cross contamination providing evidence that it works (supplementary information).
- 3) Page 5, line 97: Please explain how you took into account the changes in the internal pressure of the cylinders and their potential fractionation effects? Instrument performance
- 4) Page 6, line 110: "machine working gas" is not defined. In Figure 3. The term Ref/Working gas is used. Is it the same?

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5) Page 6, line 116 is stated: “The precision became significantly worse for all species but isotopologue 627 in the time period between September 2017 and July 2019 due to a gradual but significant decrease (of about 50%)” In Page 6, line 127 is stated: “Hence, we were able to clean the mirrors and retrieve $\delta^{13}C$ ”
Questions: o When exactly were the mirrors cleaned? o Which measures were affected? o What was the short and long term effect on the measurements with a timeline instrument response? o What was the effect of introducing moisture and ethanol for the cleaning of the mirrors, short and long term effect?

6) Page 9, line 199: the three experiments performed over the last two years means: before or after the cleaning?

7) Cross contamination and drift are only considered as uncertainties components on the instrument performance. However the instrument was used to measure cylinders and flask that could have important differences in matrix composition. What was the pressure broadening effect on the CO₂ measurements?

8) What is the real contribution of various components of the air, temperature and pressure variability into the instrument? Uncertainty analysis is missing.

9) Page 8, line 160 is stated: “A sensitivity analysis was performed and showed that this is such a small amount that scale effects due to cross-contamination are well below the precisions found in this study” Where is the sensitivity analysis? This an important effect and evidence should be shown to sustain this statement.

10) How the uncertainty of the method is constrained by the uncertainty in the reference values of the CO₂ mole fractions in the calibration standards?

11) What is the effect of diluting pure CO₂? Uncertainty in the mole fractions related to this? What is the contribution of the loss of CO₂ on the wetted surfaces and the emptying of the flasks?

12) Page 10, line 224: “..the known CO₂ mole fraction of the working gas..”: “mole

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fraction” is the quantity referred to in the paper. The proper unit would be $\mu\text{mol}/\text{mol}$ rather than ppm.

13) Figure 5 shows the experiment 1,2 and 3 that correspond to different measurements carried out in 2017, 2018 and 2019. The authors stated in page 6, line 116 that “the precision became significantly worse for all species but isotopologue 627 in the time period between September 2017 and July 2019 due to a gradual but significant decrease (of about 50 percent) in the measured laser intensity over that period”. Why do the error bars in 2017, 2018 and 2019 measurements look the same for the mole fraction range 400 to 460 ppm?

14) Page 12, Figure 5: Why there no uncertainty bars in x-axis? Where are the confidence bands that could support the statements?

15) Page 14, line 269: is stated “In our lab CO₂ in air samples of the same isotope composition but deviating CO₂ mole fractions are prepared manually, introducing again uncertainties, and doing these experiments regularly is therefore labor- and time intensive”. However no uncertainty budget (assessment) considering all the uncertainty contributors for the manual preparation is shown. As a minimum, it is likely that air composition affects CO₂ measurements and this is recognized latter in the text, line 291.

16) Page 14, line 275: the reference cylinders are mentioned for the first time in this section but those are not identified (serial number) neither their composition (air matrix). The same issue with the air samples used.

17) Page 14, line 285: A brief description of the gaseous reference materials is given in this section 3.2 with additional information page 15, line 302 and Appendix B. Nevertheless it is essential to have as much as information as possible on the reference materials for allowing the readers to reproduce such experiments.

18) Page 14, line 287: The author specify that ”two tanks that are specifically used

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for CMFD corrections. These latter two consist of a high mole fraction reference tank (HR) and a low mole fraction reference tank (LR) covering a great part of the CO₂ mole fraction range occurring in atmospheric samples”

Such range is: 342.8 to 423.77 ppm. However in Page 9, line 195 the author state: The SICAS is designed for the measurement of atmospheric samples of which the relevant range of CO₂ mole fractions is 370 – 500 ppm, and experiments were therefore for the most part conducted in this range.

The author can only warrant that the CMFD corrections of the instrument following the method proposed is valid for the range 342.8 to 423.77 ppm, not higher since there is no evidence for that.

19) Page 15, line 317: It will be important for the robustness of this paper to list, and assign an experimental uncertainty, to each of the uncertainty sources cited in this section “small leakages or other gas handling problems might be introduced”.

20) Page 15, line 304 . The claimed standard uncertainties on the gas tanks that were produced in-house from dry compressed natural air, “HR 423.77±0.01 ppm” and “LR 342.81±0.01ppm”, are very unlikely (considering that $Y = y \pm U$).

During the CCQM K120.a international comparison only one laboratory submitted comparable uncertainties (NMIJ) but considering potential effects of adsorption of a proportion of the molecules onto the internal surface of a cylinder and valve a limit on the uncertainties claimed by participants contributing to the reference values on this comparison was fixed to 0.095 $\mu\text{mol mol}^{-1}$ meaning that any uncertainty claim smaller to this value was replaced by 0.095 $\mu\text{mol mol}^{-1}$ to calculate reference values.

The claimed standard uncertainties from the gas tanks in this work are even half of the NOAA (real air mixtures) submitted uncertainty for the CCQM K120.a international comparison.

(https://www.bipm.org/utis/common/pdf/final_reports/QM/K120/CCQM - K120.pdf)

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21) Page 16, Table 5. define what are CO₂ err, $\delta^{13}\text{C}$ st. err., $\delta^{18}\text{O}$ st. err. and their units. It appears very unlikely that calibrated reference materials of CO₂ in air are provided with an uncertainty equal to 0.01 $\mu\text{mol mol}^{-1}$. Therefore CO₂ err is most likely a precision. Please justify why the precision is the only uncertainty contributor that matters by proper considerations on the goal of the experiment.

22) Page 17, line 368: The statement “The mole fraction (X) of the four most abundant isotopologues of a measured CO₂ sample are determined using two reference gases with known CO₂ mole fractions and isotope compositions” must be completed by including:

- A phrase stating that the measurements are only valid for the range of 342.81 ppm to 424.52 ppm (according to Table 5, page 16) since the standards must bracket each of the three expected isotopologue mole fractions in the samples;

- an uncertainty budget including at least two components, the first related to the repeatability of the measurement results (MPI-Jena), and the second related to the stability and homogeneity of the isotope ratio values in different standards containing nominally the same CO₂ gas;

- It is also crucial when proposing a calibration procedure to consider the uncertainty of the calibration standards. The uncertainties on the reference isotopologue mole fraction values need to be first estimated, and then used in an uncertainty budget reflecting a two point calibration process for each isotopologue.

23) The term “reference gases” is not clear into the document. It is first mentioned in

- Page 17, line 369; “The CO₂ mole fractions are chosen such that normally occurring CO₂ mole fractions in atmospheric air are bracketed by the two reference gases”

- in Page 17, line 348: “. . . We developed a calibration method based on the idea that including the measurement of two reference gases covering the CO₂ range of the measured samples (in our case LR and HR) enables the correction of the measured

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isotope ratios...”,... then;

- In Page 17, line 371: “..Due to the broad range of CO₂ mole fractions that are covered by the reference gases, measurement of both working standards will enable the calculation of the (linear) relation of the measured mole fraction (X_m) and the X_a,..” .. then in;

- Page 24, line 506: “..we used natural air as reference gases (or air mixtures close to natural air)”

- but then in Page 5, Figure 3: Ref 1 and Ref 2 appears without being defined elsewhere in the document and the Ref/Working gases term as well.

So are Ref 1 and Ref 2, the reference gases? Same as listed in Table 5 as LR and HR (Page 16)?

Which gases are the Ref/Working gases?

Please define; reference gases, measured samples, reference cylinders, calibration gas mixtures, Āask samples, HR cylinder, LR cylinder, Ref Working gases and machine working gas.

24) Page 17, line 370: Is Appendix 1 or Appendix A?

25) Page 18, Table 6. No units?

26) Page 19, line 407: when was the sausage series 90-94 measured in 2020 (month exactly?)

As described in Page 20, line 434. There was an important long term effect of the aliquot storing during 3 to 20 months for $\delta^{18}\text{O}$ measurements and this could strongly influence the conclusions of this intercomparison.

27) Page 20, Table 7. No units? Why comparing the difference SICAS-MPI with NOAA-MPI? Which technique was used by NOAA?

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28) Page 22, line 440: figure 8 shows results outside the mole fraction range validated in this work (343-425ppm). No conclusions can be stated for measurements outside the range.

29) Page 24, line 491: The author state “In this study we show that WMO compatibility goals can be reached with our Aerodyne dual-laser absorption spectrometer for stable isotope measurements of atm-CO₂ in dry whole air samples if the instrumental conditions are optimal and there is no uncertainty induced because of gas handling procedures (flask sampling for instance)” but unfortunately no uncertainty budget was shown in the paper to underpin this statement.

30) Page 24, 496: The author state “Non-linear dependencies on the CO₂ mole fraction occur for measured isotopologue abundances but are insignificant in the typical ambient CO₂ mole fraction range“ This is relatively true if compared to the compatibility goals.

31) Page 24, line 510: The author state “From studying the results of the QC we conclude that precisions are significantly better for the RM, while measurement stability is very similar, both for the δ 13C and the δ 18O measurements.”. With the current version of the paper, there is no evidence to show that the isotopologue method was applied correctly, using proper reference materials and proper measurement sequences which would ensure frequent drift corrections and two points calibration for each isotopologue. If the isotopologue method is kept after revision, and if the same observations are made, consider explaining why the two methods provide different precisions.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2020-365, 2020.

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