We would like to thank the Referee for the constructive comments and helpful suggestions on the manuscript, which helped us to further improve the clarity of the paper. Below, we give detailed responses (in blue) where appropriate.

Anonymous Referee #1

General comments:

Unfortunately, despite the promising title, abstract and introduction, this study provides more questions than answers. The reader is not told until L53, after an Introduction loaded with information related to the Oldest Ice challenges that this study only reports on the development of a new laser spectrometer for multiple gas analytes. This study does not include any information about the sublimation technique, i.e., how the gas sample will be extracted from the ice. This makes it impossible to assess the potential efficacy of the system for ice core measurements, which makes the last sentence (L377) seem a little premature, and the title, abstract and introduction seem misleading. (...) the instrument is a long-way from being well-suited to ice core analysis. In particular, the section beginning at L337 focuses on one of the challenges of using laser spectrometers for small gas volumes – that the volume of gas must be kept constant. Figure 10 nicely shows the problems this causes for the measurements. As the sublimation system is not described and no results reported, it is difficult to judge how effectively this problem will be dealt with via the calibration method suggested.

We regret that the Reviewer was misled by the title/abstract of our manuscript and we apologize for not meeting his/her expectations. In the revised version, we make clear very early on, i.e. in the abstract and the introduction, that this is only the first of two papers on this topic. The second paper will describe the sublimation extraction in detail and will be submitted next year. However, a thorough description of the QCLAS itself, as done in this manuscript, is already a formidable challenge and easily fills one manuscript. The multi-species capability of our unique dual-laser instrument and its unmatched performance for small air samples of only 1 ml STP in batch mode with similar or even better performance than off-the-shelf spectrometers in through-flow mode and high sample pressures, in our opinion represents a substantial scientific progress and easily justifies publication on its own. Regarding the issue of pressure adjustment, we accentuate in the revised manuscript that (i) using our calibration we can correct for the pressure dependence and (ii) that we designed our QCLAS inlet system in such a way that we can adjust the pressure of our standard gases to the pressure of the ice core derived sample within 0.04 mbar. Moreover, our multi-gas calibration routine ensures that we always have a standard gas that is similar in concentration and carbon isotopic signature to the sample derived from the ice cores. This implies that the important issue concerning the size of the ice core sample is already solved.

At two points I felt that more technical information could have been provided: L83 on the selection of absorption lines, and~L102 on the beam characterization. The figures are all clear and helpful and the paper itself is well-written.

Added a table with the information about the selected absorption lines. Values for the beam waist and the optical power were also added to the main text.

Other comments:

Abstract L10: Where are these precision values from? I can't find their origin in the manuscript. Values at L288 are different. Please state that these are 1 sigma values, if that is the case.

There was a mistake regarding the precision values for N_2O and CH_4 . They should read as given at L288 as pointed out by the Referee. Replaced the wrong values and added the information about the 1σ .

L11: How do "Repeated measurement cycles of air samples" demonstrate "an excellent accuracy level"?

We realize that this statement was difficult to understand in the given context. We were referring to repeated calibration runs, which agreed very well within the instrument measurement uncertainty. The wording was changed accordingly.

Introduction: Nice summary of modern measurements and the Oldest Ice campaign but it doesn't provide much context for this technical study on spectrometer design.

The instrumental development with its specific design has been fully driven by the ice core project, and it is important that this becomes clear in the introduction. Nevertheless, we are thankful to the reviewer for his feedback, and we revised our manuscript to inform the reader early (both in the abstract and the introduction) that this paper describes the QCLAS development.

L68-71: Both studies cited here use Picarro instruments that do not utilize cavity-enhanced technology.

The Picarro instruments are based on cavity ring down technique, and the signal is enhanced through the cavity length. Therefore, it is correct to refer to as cavity enhanced technology in this context.

L77-78: How were these values chosen? Are they 1 sigma values?

Added to the manuscript: " In order to allow for authoritative interpretation of the observed glacial/interglacial changes in the biogeochemical cycles of these three greenhouse gases, a signal-to-noise ratio of better than 5 for the centennial to multi-millennial variations found in ice cores for CO₂, CH₄, N₂O, and $\delta^{13}C(CO_2)$ over the last glacial cycles is required. This results in precision targets of these parameters for high-quality ice core analyses of 0.5 ppm, 2 ppb, 2 ppb, and 0.04 ‰, respectively. These targets are either comparable or better than the best ice core analysis systems available to date."

L151: Last sentence is repetition.

To avoid confusion we rephrased this sentence: "*Thus, this concept allows for a simpler alignment mechanism and hence it also minimizes the dead volume behind the rear-mirror that would be required otherwise.*"

Section 3.1, L255, sentence beginning "Our setup..." I didn't catch the meaning here.

To clarify the text, the following modification was applied: "*Currently, custom-made MPC requires about 300 s to be completely evacuated and subsequently filled with another gas. This relatively rapid exchange time is due to the improved leak-tightness and minimal surface interactions, and it is well within the constrain defined by the Allan variance minimum.* "

L258: Can the authors further explain why d13C-CO2 and CO2 behave differently to the other analytes during the Allan-Werle test? Why do the d13-CO2 measurements drift significantly when the others do not?

The $\delta^{13}C(CO_2)$ is a ratio given by the two measured quantities of ${}^{12}CO_2$ and ${}^{13}CO_2$ and, therefore, the random errors of these quantities sum up in the ratio. Furthermore, the $\delta^{13}C(CO_2)$ is also temperature sensitive as now mentioned explicitly in Sect 2 in the context of line selection. See also our reply to the comments of Referee #2. To clarify this detail we added the following text:

"This different behavior of $\delta^{13}C(CO_2)$ can be understood by considering the facts that i) this quantity is a ratio between two measured quantities of ${}^{13}CO_2$ and ${}^{12}CO_2$, therefore, the random errors of these quantities sum up in the ratio, but correlated drifts are eventually eliminated, and ii) the $\delta^{13}C(CO_2)$ is highly temperature sensitive as discussed in Sect. 2 in the context of line selection."

L270-271: The Allan-Werle shows the optimum time to integrate the data over to obtain high precision. How does this ensure high accuracy?

If one can measure a reference gas right after the unknown gas sample was analyzed and keep this alternating measurement cycle within the time period defined by the averaging time corresponding to

the Allan variance minimum, then the accuracy can be as high as the precision, assuming that the reference is accurately known. In other words, precision is a necessary but not a sufficient prerequisite for accuracy.

Figure 9 and associated text: Much of this underestimation of all the analytes is attributed to optical saturation...this seems to be a significant problem because the off-set changes with pressure. What is preventing you from reducing the intensity further? The 'neutral density filter' mentioned at L118 doesn't seem enough here.

We already reduced the laser initial intensity by a factor of 10. Further reduction would lead to a decrease of the SNR because of detector noise, which then would negatively affect the precision. For the targeted precision, we have to make this compromise between enough signal and potential optical saturation. In any case, our calibration routine takes care of systematic effects introduced by slight optical saturation. These details are now included in the revised manuscript.

Anonymous Referee #2

General comments:

(...) I believe that the performance of the spectrometer could have been improved by improving the fit routine, therefore I suggest to the authors to explore this suggestion. This hopefully would not require them to redo the analysis, if they saved data for playing with the fit parameters at posteriori. However, I would say that this is not compulsory since the authors seems to have achieved the target precision on the measurements (although it would further improve the precision, and it would perhaps allow to remove or at least minimize the corrections on the pressure and concentration dependencies). I therefore recommend this manuscript for publication on AMT, after considering the comments below.

We fully share these thoughts with the Referee. Using more sophisticated line profiles in the spectral evaluation has the potential to reduce the current pressure dependence, but most likely the impact will only be marginal. At the moment, however, we don't have a fitting routine going beyond the Voigt-profile, but we are working on implementing the HTP-profile fitting algorithm in the near future. One serious issue here is, however, the four missing line parameters for the molecular transitions. Neverthe-less, the raw spectra have been recorded and they can be post-processed later, once the parametrization is available. This aspect is now included in the conclusions as further potential for future improvement.

Specific comments:

The whole story regarding the absorption line saturation need more discussion in the paper. Authors should mention the optical power in the multipass cell as well as the beam waist. With those two parameters, the optical path length and two parameters available from the HITRAN database (the Einstein coefficient and the degeneracy of the excited state) they should be able to estimate the saturation parameter (s), which is the ratio between the intensity (I) used and the saturation intensity (I_sat) that is calculated. Then, the difficulty to find the exact saturation effect is due to the fact that it depends on the regime "homogeneous" (Lorentzian broadening dominate) or "inhomogeneous" (Gaussian broadening dominate). But authors could calculate this assuming that at 5 mbar they are in the inhomogeneous regime. Authors should therefore calculate their saturation intensity (I_sat in W/cm2) and $s = I/I_sat$, and therefore the effect of saturation on the absorption lines. Then they should check if this value can be in line with an estimation of the amplitude stability of their laser source. (A good reference for saturation spectroscopy is Giusfredi, et al.: Theory of saturated-absorption cavity ring-down: radiocarbon dioxide detection, a case study, J. Opt. Soc.Am. B, 32(10), 2223, doi:10.1364/josab.32.002223, 2015).

We agree that the saturation parameter could be roughly estimated, but this will not help us improving our instrument performance. Based on experimental evidence, we know that for sample pressures above 10 mbar the saturation is negligible (< 0.2 %). The same is true for further reduced laser intensity (<

1mW). However, the gas pressure is defined by the sample availability. Therefore, we expect the gas pressure to be \leq 5 mbar. Unfortunately, a further reduction of the laser intensity has a negative impact on the SNR, i.e. on the analytical precision (see also our reply to Reviewer #1).

Nevertheless, the well-founded remark of Reviewer 2 motivated us to have a closer look at the saturation effect by (i) comparing absorption profiles, recorded at a fixed gas pressure, but with two different laser intensities, and (ii) by changing sample pressure at fixed laser intensity. From these empirical data, and assuming the inhomogeneous regime as proposed by the Referee, we estimated a saturation intensity and thereof the saturation factor s of 0.014. This effect can account for about 0.7 % reduction in the line absorption. Given the discrepancy between observed and estimated values, we checked the input parameters of the fitting routine and found a mistake in the pressure conversion (hPa to atm). Thereby, a systematic bias of 2.6 % was introduced to the retrieved concentrations. Since this mainly affects the calibration factors, we re-calculated these values and also added a short paragraph about the saturation. The revision in our pressure value and calibration has no further implications for the quality of our measurements.

We are very thankful to the Referee for drawing our attention to this issue.

L51-52. In the paper you mention about discrete measurements in ice-core and here you mention a continuous extraction system. Please be more consistent on this point. And if possible, please refer to a paper "in preparation" for the extraction technique.

Text revised to: "In this publication, we will present in detail the laser absorption spectrometer and its performance, while the continuous sublimation extraction system providing a cm-scale vertical resolution will be described in a separate paper (Mächler65et al., 2020)."

L84-85. In the selection of the absorption lines did authors take into account the temperature dependency of the absorption lines? This should be then discussed in the manuscript.

Yes. Added a short paragraph on this topic in the revised paper.

Figure2. This wiggled shape in the residual is very large, I think authors should consider using a different line-shape profile which would include Dicke narrowing and perhaps also speed dependence collisional broadening. The intensity of the peak absorption is only 150 time higher than the peak-to-peak on the residual, which is in with the 11 permil precision on a single spectrum. But this also show that on the d13CO2 precision authors are limited to those wiggles and that they could further improve their meas-urements. Furthermore, looking at HITRAN2016 simulation the intensities at 5 mbar and 20°C do not seems to have the same intensity as showed here. Is there an error in the HITRAN database? If so, authors could mention it in the paper and say which line has the wrong cross-section and by how much is wrong (based on their gas standard mixtures). Last, they should be mention that this is a single scan spectrum (acq. Time 75 us). What is the strategy then? How many spectra the authors average before perform the fit? This should be also mentioned.

See above our reply to the general comments. Our midterm goal is to implement the HTP-profile fitting algorithm for spectral evaluation. However, this will mainly remove systematic biases, i.e. improving accuracy rather than affecting precision. Furthermore, as we use the integral of the absorption profile instead of the peak amplitude, the situation is much more relaxed as the integral over the residual is approaching zero. The current performance allows us to reach the precision targets, but we have to perform careful calibration to achieve the required accuracy. The information about spectral averaging is given at line L190 and a link to Fig.2 is provided at L196. Added sentence on future potential development in spectral analysis in the Conclusions.

L116-119. Please provide the power injected in the MPC. Are authors not annoyed by optical fringes from the ND filter?

The laser power after the ND filter entering the MPC is 5.4 mW. The ND filter was custom-made using a wedged substrate. This reduces the unwanted etaloning effect and the remaining modulation is as broad

as our spectral coverage. Nevertheless, mechanical and temperature effects still may affect the instrument long-term stability. Therefore, we use a water-cooled optical plate, stabilized at 5 mK, and a hermetically sealed housing around the optical module. We added this information to the manuscript.

L121: how the accuracy on the temperature was measured? With an independent temperature probes? is this the accuracy of the temperature stabilization or just the precision of the temperature sensor itself? Please specify. This could then be related to the temperature dependency of the absorption lines and to the achieved precision on the d13CO2.

The base-plate temperature was measured indirectly based on the T-sensor included in the thermochiller used to circulate the cooling liquid. The gas sample temperature in the MPC was measured by high-precision NTC sensors, which were not calibrated in our laboratory and may have some bias (~0.5 %), while their precision is much better (mK). The temperature effect on $\delta^{13}C(CO_2)$ can be easily estimated considering the lower state energies of the involved transitions, which results in a temperature sensitivity of ~16 ‰/K. Although it may be difficult to maintain long-term stability of the absorption cell to better than 0.05 K, changes in the cell temperature can be measured with a precision on the order of mK using high-precision thermistors. Since the measured temperature is used continuously for interpreting the absorbance spectra, the temperature dependence of the line strength is not a major impediment to obtain isotope ratio precisions better than 0.02 ‰ for d13CO2. We added this information to the manuscript.

L130-131. What about for the d13CO2? It is weird that author fixed they required optical path length based on the CH4 and N2O required precision rather than on the d13CO2 measurement.

Fig.2 shows the absorption of the different species with their corresponding axes (left and right). Please note the scaling difference between these axes. The CH4 and N2O absorptions are less than 0.5%, while those for CO_2 are about 60 %. This clearly shows that the required optical path length was mainly driven by CH₄ and N₂O. We changed the wording to include this detail.

L139. Significantly longer. Could you provide a value?!

Up to several hours. The required duration was strongly dependent on the conditioning history of the cell, but even by baking, purging, and evacuating the cell over few days the pump-down time of the cell after filling with a sample gas took more than 20 minutes. This information has been added to the manuscript.

L155-156: How authors can simulate the frequency of the optical fringes produced by the multiple passages?! It is just a maximization of the distance between the neighboring spots as mentioned few lines below or is something else?

Yes, but not only. Besides the lowest possible overlap of the individual reflection spots, we also take into account the optical path difference of the neighboring spots and try to avoid those patterns where the interference fringe frequency generated by the optical path difference is comparable to the width of the absorption line. Especially, overlaps of the beam spots with small pass number (e.g. 4 and 6) differences are problematic. Searching for patterns that mostly fulfil these criteria is expected to result in a reduced optical fringe level or at least have less impact on the absorption line retrieval. These considerations have been added to the manuscript.

L203. Critical orifice. Can authors mention the size? Well, in flow measurement this would probably fractionate...please explain.

Added a short text to clarify this issue: "The critical orifice size (20 μ m) as well as the output pressure of the regulators were all carefully selected to avoid isotopic fractionation as the gases flow through the system. A series of experiments was conducted in flow-through and static regime to investigate potential fractionation effects due to flow-restriction elements such as critical orifice and the optional metering valve

used in the flow-through mode. Their effect was found to be lower than our detection limit. With this setup it is possible to operate the instrument both in flow through or in batch mode for discrete samples."

Table 1. When second digit precision is reported (eg. 0.01) then concentration should be reported with the same number of digits (eg. 248.8x ppm). Did authors monitor their standard mixtures over time? Do they see any drift?

Added the second significant digit to the values.

Figure 7. It would be interesting to see the same AW statistical analysis for a static experiment. Can authors add this information? Since the ice core measurements will certainly done using discrete samples and in static mode, I guess.

We performed several experiments of this kind, also because we had the same concern as the Referee. These tests resulted in very similar precision values as those conducted in flow-through mode. Of course, in this case we had to limit the measurement period to shorter time (< 1 h), to avoid drift effects caused by surface effects. The performance in batch mode is also demonstrated by the following sections of the manuscript, where we systematically focused our attention on discrete samples and demonstrated analytical performance obtained using such 1 mL samples. In our opinion, these data are more informative then showing a replicate of an Allan-Werle plot.

L281: This sequence is repeated several times: Can authors provide information about the frequency of those 50 measurements?

The time required to measure consecutive sample/reference pairs was 10 minutes, thus, for the 50 repetition cycle, 8.3 hours was necessary. We added this information to the revised manuscript.

L293-294. "Even for discrete samples...". What do they mean with this sentence? Because for a single discrete measurement the performances are maintained for a time given by the AW analysis, which is shown only a maximum integration time of 16 minutes. What authors mean with this 24h of continuous operation? Can they prove it with an AW plot?

Individual or discrete gas samples can be measured with a precision as determined by the AW analysis. However, when switching between sample gases collected in dip-tubes further additional artifacts/biases, mainly originating from gas handling, can affect the accuracy of the measurements. Of course, during the time that is required to replace the sample gas with the next sample the spectrometer can drift. However, we demonstrate that with our cyclic measurement approach, i.e. quickly alternating between dip-tube sample and reference gas measurement, these drifts can be accounted for and thus their effect can be minimized even for longer periods of time, e.g. 24 h. Figure 8 demonstrates exactly this situation.

L311-312: "This two-point calibration..." This is normally not a linear relationship, but rather an exponential with discrepancy becoming larger and larger at low concentrations...It is possible that authors would be able to approximate it to a linear relation in the range of concentrations they will have in the ice cores? Why authors did not just apply different dilution factors to on of their standard to study this effect on a larger concentration range? Just to mentioned, I see an artefact of 0.94 permil on the working range of 157.7 - 345.5 ppm, which is more the 20 times larger than the claimed accuracy.

In our experience, the linear relationship is a very good approximation (see also the fit residuals on Fig.9) for such a narrow concentration range. We did several measurements in the past using the dilution approach as also suggested by the Referee, and we always found a tight linear correlation even for various molecular species, e.g. Tuzson et al., Appl. Phys. B 92, 451–458 (2008) and Waechter et al, Opt. Exp. 16, 9239-9244 (2008). Our focus was only for the concentration range expected for ice core samples, because this is the main application for which we developed the instrument and which we fully cover with our custom-made standard gases. The dilution is feasible, but it is a time-consuming process that

we want to avoid when analyzing ice core samples. That's why we opt for a robust two-point verification approach. Unfortunately, we are unable to follow the Referee regarding the artefact.

Figure 9. So, if I understand well, the difference between the measured and the reference corresponds to the difference between the measurement done by the commercial instruments used for calibrate the standard gas mixtures and your new instrument, is that correct? But, you should say what is your approach for your instrument. Do you stick with the intensities provided by HITRAN database or you calibrate the spectrometer with one of the standard bottles? Because if it is the second option, then you should have at least one point which would match well the reference measurement. And what about the d13CO2? Because for that you have to rely on a reference measurement. So, I do not get why there is this offset between reference and measurement for all isotopic ratios rather than a crossing point.

Yes, that is correct. The concentration of the trace gases in the reference cylinders were determined using the WCC instrumentation, while the $\delta^{13}C(CO_2)$ values were determined by IRMS, as described at L240-L243. The raw values reported by our spectrometer are purely based on spectroscopic (HITRAN) and physical parameters (OPL, T, and P) without any additional calibration. In the case of the $\delta^{13}C(CO_2)$ the same approach was used, but included the scale conversion from natural abundance used by HITRAN and the *Rs* value defined by the VPDB-scale. Finally, a constant offset of 9 ‰ was added to bring the "spectroscopic"-scale closer to the VPDB values. This last step could also be included in the calibration function. The calibration curves in Figure 9 then illustrate the conversion of the instrument values to international scales. We revised the corresponding paragraph to include these details.

L343. "This indicates that..." You should explain your approach here. I believe that you leave the Lorentzian contribution on the absorption lines free to adjust with pressure. This should be mentioned in the text. As well as that the concentration in mixing ratio is then corrected for the total gas pressure in the cell. I believe that the artefact you see could be removed (or at least minimized) by changing the fit profile as mentioned above.

Exactly, the Lorentzian width is calculated based on the actual pressure readings and using the pressure broadening parameters γ_{air} while the concentration is determined using the ideal gas law. We added this information to the manuscript. We also think that the artifact shown in Fig. 10 could be reduced by using a more appropriate line profile model that includes at least the Dicke narrowing term. Further contributions can be due to the uncertainties in the pressure broadening coefficients, line strengths and frequency scaling as well as optical saturation.

L345. Can authors estimate the dependency for d13CO2 around 5 mbar? what precision in pressure is required the 0.04 permil precision and how it compares with your accuracy on the pressure measurement?!

Yes, the dependency of $\delta^{13}C(CO_2)$ on pressure around 5 mbar is 0.81‰/mbar, thus we need 0.05 mbar accuracy on the pressure measurement to achieve 0.04 permil precision on $\delta^{13}C(CO_2)$. Our pressure sensor has a stated accuracy of 0.2% of the measured value, i.e., an uncertainty of 0.01 mbar for the 5 mbar sample pressure. We included this information in the revised manuscript.

L356: "possibly at value > = 5 mbar." Here you should rather report 5 +/- xx mbar, with the error estimated in order to stay within the 0.04 permil (comment above). Done.

L370-371: mention that those are 1 sigma precisions. Done.

Technical corrections:

L9. I would rather call it multi-pass absorption rather than direct absorption (or directmulti-pass absorption if authors want to keep the word direct).

We do not agree. The technique used here is the direct absorption spectroscopy, while the multipass is just to enhance the signal.

L61-80. This part should go to the introduction rather than in the methods. The latter should be focus on the description of the methods.

We agree and implemented the suggested changes.

L108. Mention the photodiode model. Done.

L173. I suggest By applying. Done.

L293: replace "targets" with "target performances" Done.

Interactive comment by Thomas Bauska

I found the paper very interesting to read throughout but had one question constantly in the back of my mind: how will the instrument deal with the presence of ice core drilling fluid in the gas sample? Of course, we do everything we can to avoid this and there are ways to mitigate the problem (that are beyond the scope of this study). I was thinking more along the lines of whether this was considered during the design phase. Or if the author's have been able to do theoretical or experimental work on potential spectral interferences. That's all. If drilling fluid can be shown not to be a problem, than the method will have (another) major advantage on dual-inlet IRMS measurements of carbon isotopes as drilling fluid can be the Achilles' Heel of this technique. However, if drilling fluid is problematic, it's not clear to me if traditional GC-MS techniques remain better suited for small samples.

Yes, we are well aware of this highly challenging issue and therefore we clarified beforehand the expected type of the drilling fluid that will be used within the "Beyond EPICA Oldest Ice Core" project. We will add the following lines to the manuscript:

"A significant advantage of laser spectrometry over - for instance - mass spectrometry is that the absorption lines are gas-specific and interferences between different gases unlikely. In the case of ice core analyses, in particular, the use of organic drill fluids may lead to contamination with potentially absorbing trace gases. Therefore, we tested for interferences with the drill fluid (ESTISOL[™] 140) which is to be used in Antarctica within the Beyond EPICA ice core project. We purchased pure ESTISOL[™] 140 and introduced the headspace of drill fluid contaminated sample into the multipass cell in quantities that we considered representative for the ice core samples. This lead to no alterations in the spectrum within the wavenumber window covered by our two lasers. The main reason is that these large organic compounds have very broad absorption features and tend to be localized to frequencies typical for functional groups. Therefore, our narrow-band laser spectroscopic approach in the mid-IR is not affected by such contaminations in the studied wavenumber range."

High precision High-precision laser spectrometer for multiple greenhouse gas analysis in 1 mL air from ice core samples

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Abstract. The record of past global background atmospheric greenhouse gas composition from ice cores is crucial for our understanding of global climate change. The "Beyond EPICA Oldest Ice Core" project is currently pushing the frontier of this knowledge forward by the retrieval of an ice core reaching back to Future ice core projects will aim to extend both the temporal coverage (extending the time scale to 1.5million years ago. The oldest section of this core will have been strongly thinned by

5 glacier flow with about 15 kyr being trapped in as little as 1 m thickness of ice. This reduces the available sample volume to only a few mL of air for the targeted century-scale resolution of greenhouse gas records. Under these conditions, the required accuracy for multiple greenhouse gases cannot be achieved with currently available analytical methods.

Here, we present a new approach to unlocking such challenging atmospheric archives with a Myr) and the temporal resolution of existing records. This implies a strongly limited sample availability, increasing demands on analytical accuracy

- 10 and precision, and the need to reuse air samples extracted from ice cores for multiple gas analyses. To meet these requirements, we designed and developed a new analytical system that combines direct absorption laser spectroscopy in the mid-infrared with a quantitative sublimation extraction method. Here, we focus on the high-precision mid-IR-dual-laser direct absorption spectrometer. The instrument is designed to simultaneously measure spectrometer, for the simultaneous measurement of CH_4 , N_2O , and CO_2 concentrations, as well as $\delta^{13}C(CO_2)$ using. Flow-through experiments at 5 mbar gas pressure demonstrate an
- 15 analytical precision (1σ) of 0.006 ppm for CO₂, 0.02% for $\delta^{13}C(CO_2)$, 0.4 ppb for CH₄ and 0.1 ppb for N₂O, obtained after an integration time of 100 s. Sample-standard repeatabilities (1σ) of discrete samples of only 1 mL STP-1 ml STP amount to 0.03 ppm, 2.2 ppb, 1 ppb and 0.04% for CO₂, CH₄, N₂O and for $\delta^{13}C(CO_2)$, and it achieves a precision of 1.6 ppb, 1.0 ppb, 0.03 ppm and 0.04%, respectively. Repeated The key elements to achieve this performance are a custom-developed multipass absorption cell, custom-made high-performance data acquisition and laser driving electronics, and a robust calibration approach
- 20 involving multiple reference gases. The assessment of the spectrometer capabilities on repeated measurement cycles of air samples demonstrate an excellent accuracy level, and high reproducibility of the spectroscopic and the gas handling system. In addition, this non-invasive method allows discrete air samples mimicking the procedure for external samples such as air samples from ice cores was found to fully meet our performance criteria for future ice core analysis. Finally, this

non-consumptive method allows the reuse of the precious gas samples for further analysis, which opens creates new op-

25 portunities in ice core science.

1 Introduction

Precise monitoring of Precisely monitoring the current anthropogenic rise of the greenhouse gas concentrations of $(CO_2, CH_4 and N_2O)$ concentrations is essential for the implementation of the Kyoto (UNFCCC, 1998) and Paris (UNFCCC, 2015) agreements, with their goal to substantially mitigate greenhouse gas emissions and limit global anthropogenic warming to well below

- 30 2°C relative to the pre-industrial era. Several. Therefore, several monitoring networks have been established, comprising both ground- and satellite-based instrumentation for accurate greenhouse gas measurements to accurately measure the greenhouse gases with high temporal and spatial resolution. For ground-based monitoring, where essentially unlimited sample volumes volumes of sample are available, continuous infrared spectroscopic analysis gained is gaining increasing importance, as it allows for high time resolution with a minimum of sample preparation and multiple greenhouse gases in a single instrument (e.g.
- 35 McManus et al., 2010; Hammer et al., 2013; Hundt et al., 2018). In recent years, these techniques have been further developed, also enabling isotopic measurements of CO₂, CH₄ and N₂O (e.g. Tuzson et al., 2011; Prokhorov et al., 2019; Eyer et al.; Ibraim et al., 2017).

While today Today's changes are precisely monitored with constantly improving global measurement networksand provide , providing strong constraints on anthropogenic and natural emissions. However, such direct atmospheric observations only

- 40 began in the late 1950s (Graven et al., 2013). However, for validating climate models that predict Earth's future climate, , and therefore, other sources for data, such as temperature and greenhouse gas concentrations, from a larger time span, i.e. over many centuries to millennia, are neededgases, are needed to validate and constrain climate models when covering many centuries or even millennia. Moreover, processes controlling the natural range and variability of greenhouse gases can only be fully identified assessed when the greenhouse gas record is extended over the full range of climate variations, representative
- 45 of long-term <u>centennial</u>, <u>millennial</u>, orbital up to weathering time scales. An extension of the observation record, spanning the last 800 kyr, has become possible using polar ice cores, from which small samples of past atmospheric air can be extracted. Thus, a reconstruction of the CO₂, CH₄ and N₂O records over the entire anthropogenic era (Rubino et al., 2013; MacFarling Meure et al., 2006) and further back in time over past glacial-interglacial cycles covering up to the last 800 kyr was realized (Loulergue et al., 2008; Schilt, 2013; Bereiter et al., 2015; Petit et al., 1999; Lüt
- 50 . Apart from greenhouse gas concentrations in ice cores, which are often determined by GC techniques, the precise quantification of their isotopic composition using mass spectrometric (MS) or coupled gas chromatography mass spectrometric (GC-MS) analyses of ice core samples has become possible in recent years (Schmitt et al., 2012; Schilt et al., 2014; Bock et al., 2017; Bauska et al., 2018). However, these methods involve tedious and time-consuming separation of individual gas species from the air matrix. As an alternative approach, the application of a mid-IR tunable diode laser spectrometer for discrete CO₂ analyses on
- 55 ice cores had been pioneered at the University of Bern in the 1970s (Lehmann et al., 1977; Neftel et al., 1982). This technique avoids the separation of CO₂ from the gas matrix and enables concentration measurements on small (<10 g) of ice samples

(Bereiter et al., 2015; Güllük et al., 1997, and references therein). Recently, cavity-enhanced near-IR laser spectroscopy was applied for continuous online measurements of CH_4 in ice cores (Chappellaz et al., 2013; Rhodes et al., 2015). However, as these analyses involve a gas separation step from a continuous water stream, solubility effects require external calibration of such melt water based online measurements.

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In 2019, the European "Beyond EPICA Oldest Ice Core" project was started by partners from ten European nations with the goal to retrieve a continuous Antarctic ice core going back over the last 1.5 Myr (Fischer et al., 2013). For the first time, this ice core will allow to reconstruct the atmospheric changes that occurred over the so-called Mid Pleistocene Transition (approximately 1.2 - 0.9 Myr ago), when the cyclicity of glacial/interglacial cycles changed from 40 to about 100 kyr, and the

- 65 amplitude of continental glaciation during ice ages substantially increased. Due to glacier flow, the ice at the bottom of the ice sheet, where the very old ice is preserved, experienced extreme thinning, i.e. about 15 kyr of climate history are compressed into only 1 m thickness of ice core (Bereiter et al., 2014; Fischer et al., 2013) (Fischer et al., 2013) thus implying a limited availability of sample for greenhouse gas and other analyses. Accordingly, these Similar extreme thinning is observed in the bottom-most sections of high accumulation coastal Antarctic ice cores, which allow for temporal extension of high-resolution
- 70 greenhouse gas records. Accordingly, such extraordinary glaciological conditions require novel analytical approaches to maximize temporal resolution of the records, while minimizing sample consumption and, at the same time, making no compromises on precision and repeatability of the gas analyses. Thus, the various greenhouse gas analyses, previously done on several pieces of ice, have to be combined and the sensitivity of the analytical methods improved, and whenever possible reuse of the gas after the analysis for other analytical purposes should be pursued.
- 75 These goals motivated the our development of a multi-species laser spectrometer using state-of-the-art mid-IR quantum easeade laser (QCL) technology. This new spectrometer is accompanied by the development of a near-IR laser sublimation system to quantitatively and continuously extract novel approach that combines the high-resolution and selectivity of a laser absorption spectrometer with the quantitative and continuous extraction of the air enclosed in ice cores in 1-2 cm resolution. The sublimation techniqueand its performance will be described in a separate paper, while here we concentrate on the description

and performance of the laser spectrometer. 80

> In the following, we present the technical details of the developed instrument including the optical design, the custom-made absorption cell and electronics, the instrument periphery as well as the custom-made standard gases needed for the calibration. Finally, a detailed characterization and calibration for 1 ml STP air samples is given, demonstrating the excellent analytical eapabilities of the spectrometer, and including the first steps towards a calibration scheme that can handle the variable sample

volumes and pressures that are expected from ice core samples. 85

2 Methods

Discrete measurements of greenhouse gas concentrations in ice cores often rely on GC techniques, while isotope ratio analyses are performed by mass spectrometry. However, these methods involve tedious and time-consuming separation of individual gas species from the air matrix. As an alternative approach, the application of a mid-IR tunable diode laser spectrometer for discrete

- 90 analyses on ice cores had already been pioneered at the University of Bern already in the 1970s (Lehmann et al., 1977; Neftel et al., 1982) . This technique avoids the separation of from the gas matrix and enables high precision concentration measurements on very small (<10 g of ice) samples equivalent to <1 mL STP. It has been used for decades in numerous studies on concentrations in ice cores (Bereiter et al., 2015, and references therein), and has been further developed towards other-by a unique sublimation technique. In this publication, we will present in detail the laser absorption spectrometer and multi-species analytics (Güllük et al., 1997)
- 95 . Recently, cavity-enhanced near-IR laser spectroscopy was applied for continuous online measurements of in ice cores (Chappellaz et al., 2013; Rhodes et al., 2015). However, as these analyses involve a gas separation step from a continuous water stream, solubility effects require external calibration of such melt water based online measurementsits performance, while the continuous sublimation extraction system providing a cm-scale vertical resolution will be described in a separate paper (Mächler, 2020).
- In the atmospheric sciences, laser spectroscopy is a well-established analytical method for high-precision trace gas concentration and isotope ratio measurements. However, the stringent requirements related to ice core analysis still remain highly challenging. In the present study, our aim was to establish an analytical tool, which enables the <u>joint simultaneous</u> quantification of CO_2 , CH_4 and N_2O concentrations as well as the stable carbon isotopic composition of CO_2 on one in ice core-derived air sample of only 1–2 mL STP without separation of these gases from the air matrix. The required precision targets for
- 105 high-quality ice core analyses were defined as 0.1 ppm, 2 ppb, 2 ppb and 0.04% for , , , and , respectively, in In order to allow for authoritative interpretation of the observed glacial/interglacial changes in the biogeochemical cycles of these three greenhouse gases. , a signal-to-noise ratio of better than 5 for the centennial to multi-millennial variations found in ice cores for CO₂, CH₄, N₂O, and δ¹³C(CO₂) over the last glacial cycles is required. This results in precision targets of these parameters for high-quality ice core analyses of 0.5 ppm, 2 ppb, 2 ppb, and 0.04‰, respectively. These targets are either comparable or
- 110 <u>better than the best ice core analysis systems available to date.</u> Moreover, the option of cryogenically recollecting the air sample after the laser spectroscopic analysis was also foreseen.

In the following, we present the technical details of the developed instrument including the optical design, the custom-made absorption cell and electronics, the instrument periphery as well as the custom-made standard gases needed for the calibration. Finally, a detailed characterization and calibration for 1 mL STP air samples is given, demonstrating the excellent analytical

115 capabilities of the spectrometer, and including steps towards a calibration scheme that can handle the variable sample volumes and pressures that are expected from ice core samples. We stress that the sample size, gas handling and sample introduction as well as the calibration scheme presented here have been specifically designed and optimized for the use on discrete ice core air samples of 1-2 mL STP that will be provided by the sublimation extraction system that is being developed in parallel.

2 Methods

120 The targeted multi-species capabilities of our instrument is achieved by using a dual-laser concept (see e.g. McManus et al., 2011, 2015), where two distributed feedback quantum cascade lasers (DFB-QCLs) with distinct frequencies are combined and coupled into a multipass absorption cell (MPC). The lasers were selected to fulfill fundamental line selection criteria (see e.g.

Table 1. Spectroscopic parameters of the absorption lines selected for this work. The molecule *ID* (abbreviated code for isotopologues), line positions ν (cm⁻¹) as well as the lower state energies E'' (cm⁻¹), line strengths S (10⁻²⁰ cm⁻¹/(cm²molecule⁻¹)), and Einstein *A*-coefficients (s⁻¹) are from the HITRAN 2016 database (Gordon et al., 2017).

Species	<i>∐D</i>	$\overset{\nu}{\sim}$	$\stackrel{S}{\sim}$	E''_{\sim}	$\stackrel{A}{\sim}$
$\overbrace{\sim}^{12} \underbrace{\text{CO}_2}_{\sim}$	21	2301.680904	2.71	1276.4476	202.3
$\overset{13}{\sim} \overset{\text{CO}_2}{\sim}$	<u>22</u>	2302.308939	2.62	273.8809	187.8
N_2O	41	1301.684840	15.40	175.9536	<u>.6.1</u>
CH_4	<u>61</u>	1302.044313	<u>6.45</u>	219.9199	2.2

Tuzson et al., 2008) that consider regarding spectral interference issues, limitations in laser tuning capabilities ($<4 \text{ cm}^{-1}$), and achievable signal-to-noise ratio (SNR) under the targeted sample conditions. Furthermore, the selection-line selection

- 125 (see Table 1) considers the fact that CH_4 and N_2O share a region of relatively strong absorption lines around 7.7 µm, which gives access to both species within the spectral coverage of one a DFB-QCL. For CO_2 (including the two most abundant isotopologues), we use the region around 4.3 µm, with a special focus on absorption lines that have comparable intensities. In this spectral region, there are mainly two options for CO_2 that fulfill all the above our selection criteria: The lines proposed by Tuzson et al. (2008) around 2310 cm⁻¹ and the ones around 2302 cm⁻¹ that we use in this work. The latter were cho-
- 130 sen because of their higher line intensity which helps reaching the required SNR despite the small sample size. However, it should be recognized that comparable absorption for the CO_2 isotopologues means that their ro-vibrational transitions have rather different ground state energies (see also Table1). Therefore, the spectroscopically retrieved δ^{13} C-values exhibits a larger temperature sensitivity (Tuzson et al., 2008). In our case, we estimate a temperature sensitivity of the isotope ratio of about $16 \% K^{-1}$. Although it may be difficult to maintain long-term stability of the absorption cell to better than 0.01 K, changes in
- 135 the cell temperature can be measured with a precision on the order of mK using thermistors. Since the measured temperature is used continuously for interpreting the absorbance spectra, the temperature dependence of the line strength is not a major impediment to obtain isotope ratio precision better than 0.02% for δ^{13} CO₂.

2.1 Optical design of the QCLAS

- The concept and the final layout of our optical setup is are shown in Fig. 1. During the development, first a 3D CAD model coupled to ray-tracing simulations was used that allowed easy testing of different design options and optimizing beam propagation within the available space. Key factors were the beam-shaping and efficient coupling of both laser beams into the same measurement absorption cell, which is a custom-made astigmatic Herriott multipass cell (see Sect. 2.1.1)developed at Empa. Although the . The QCLs (Alpes Lasers, Switzerland) were packaged in a high-heat-load (HHL) housing housings with embedded thermoelectric cooler (TEC) and collimating lens, and the output beam properties (size and profilewas not sufficiently well
- 145 known. Therefore, the beam properties of each QCL were characterized in depth.) were characterized using a mid-IR beam profiler (WinCamD-IR-BB, DataRay, USA). The empirical values were then used to define the light sources in the ray-tracing



Figure 1. Optical layout of the dual-QCL system showing all relevant optical elements (where DC refers to dichroic mirror, ND to neutral density filter) and the optical path (colored lines) of the laser beams as simulated by <u>FRED the</u> ray-tracing software (<u>FRED</u>, Photon Engineering).

software (FRED, Photon Engineering, USA). This allowed a more realistic beam propagation along the optical path and, thus, led to better estimates for a reliable selection of the steering and shaping elements, which best fulfill the entrance conditions of the MPC (see e.g. McManus, 2007). The infrared beam is focused near the center of the cell and it's beam waist ($374 \mu m$ at

- 4.34 μ m wavelength) is closely matched to the nearly confocal cavity, such that the reflected beam maintains a nearly constant size at the mirrors while propagating in the cell. The coupling of the 7.7 μ m wavelength is slightly off from the ideal case and the realized beam-waist of 1.1 mm is about twice as large as theoretically expected. The obtained fringe level (see residual plot in Fig. 2) is, nevertheless, very low, indicating that the MPC is rather tolerant to such mismatch.
- In a first section, a beam of three lasers is generated by using a custom-made dichroic mirror (LohnStar Optics, USA) to efficiently combine the two mid-IR beams first, followed by a second dichroic mirror (Quantum Design, Switzerland) to couple in a red trace laser, which is used for alignment purposesonly. After the beam combination, the beam is split into two paths: a 'sample' path that goes through the MPC, and a 'reference' path, which is directed through a reference cell filled with a predefined gas mixture. The splitting ratio is such that the extra losses due to the multiple reflections within the MPC are compensated for, and both the sample and reference detectors (<u>PVM-2TE-8-1x1-TO8-wZnSeAR-70</u>, Vigo Systems, Poland) receive approximately the same optical power. The optical elements downstream of the beam splitting are for beam shaping

measurement cycle to obtain the laser emission profile used as signal background for the reference path.

and steering. The reference cell is mounted on a remotely controllable flip-mount, and it is taken out of the beam once per

Investigations of the beam-laser emission properties regarding intensity and frequency stability revealed an increased sensitivity of the QCLs to optical feedback when they are driven with currents near their lasing threshold (104 mA). This was



Figure 2. Example of measured transmission spectra (red), Voigt-profile fit (blue) and residual (top) for the scanned ranges at $4.3 \,\mu\text{m}$ (left) and $7.7 \,\mu\text{m}$ (right) for a gas at 5 mbar with concentrations representative of ice core samples, i.e. using standard gas #6 (see Table ???2).

- 165 more pronounced for the $4.3 \mu m$ QCL QCL emitting at $4.3 \mu m$ and led to marked instabilities of the emission frequency (jitter). Therefore, the QCLs are driven at high current (160 mA), and a quarter wave plate is placed in the front of the $4.3 \mu m$ QCL to further reduce optical feedback. High-current operation of QCLs implies increased optical output power, which is usually beneficial in terms of SNR in the mid-IR. However, in our case, the QCLs provide so much optical power (>50 mW 54 mW) that (i) the linear range of the detector is exceeded, and (ii) the absorption process in the low-pressure sample gases
- becomes saturated. To avoid these effects, a custom-made wedged neutral density filter (ND = 1.0) is placed between the two dichroic mirros(see also. This way, the optical power of both QCLs is reduced by 90% before entering into the MPC, while the transmitted optical power reaching the detector is 0.6 mW. As we will show later, this laser intensity was still not low enough to completely eliminate the saturation effect, but we refrained from further laser intensity reduction, because this would have a negative impact of the SNR value, jeopardizing the targeted precision. However it is important to note that we operationally correct for the small saturation effects within our calibration scheme (see Sect. 3.3).

To decouple the optical setup from external temperature changes, the optical breadboard is water-cooled and maintained at 20 ± 0.005 °C using a close-loop thermochiller (Oasis Three, Solid State Cooling Systems, USA). Furthermore, the whole setup is enclosed in a sealed and thermally insulated case (Fibox, Switzerland), which is purged with CO₂-free air (resulting in a stable residual background of about 15 ppm CO₂) to minimize light absorption outside the sample and reference cells. These

180 factors are significantly contributing in maintaining improving the long-term stability of the spectrometermeasurements.

2.1.1 Custom-made multipass absorption gas cell

The absorption cell is a key component of any absorption laser spectrometer. It not only defines the supported optical path length (OPL), but also the volume in which the light can interact with the molecules of the sample gas. As the SNR scales with the increase of OPL, extended paths are usually achieved by using beam folding concepts, such as multipass cells (MPCs).

185 Beam folding, however, is also an important source of optical noise in the system and needs careful consideration. In our

application, the precision targets of about 2 ppb for CH_4 and N_2O at ambient concentration and low pressure (<10 mbar) can be achieved with an estimated minimal optical path length of around 30 m. These criteria We considered these parameters as criteria for the required OPL, because of their significantly lower absorption signal compared to that of the CO_2 isotopologues (see Fig. 2 and note the different scaling in the transmission axis). These requirements are largely fulfilled by a commercially

- 190 available solution (AMAC-36, Aerodyne Research, USA), which is currently the state-of-the-art MPC for high-precision trace gas measurements (McManus et al., 2010) and which was our first choice for the prototype instrument. However, the very limited sample volume and the aim of cryogenic re-collection of the sample after measurement create additional demands on the cell: i) it must be very leak-tighton high-vacuum standards, ii) the cell inner surface must be highly inert, and iii) the cell should have a minimum dead volume-, i.e. volumes outside the optically active region. Since the AMAC-36 is primarily
- aimed at atmospheric monitoring applications using flow-through mode, the above aspects relevant for our purpose are were not fully met. This became evident when using the AMAC-36 in static mode where we observed a continuous decrease of $0.2 \text{ ppm} \text{min}^{-1}$ in the CO₂ concentration. Furthermore, despite the leak-tightness ($1 \times 10^{-6} \text{ mbar L s}^{-1}$) of the MPC, the evacuation of the cell took significantly longer compared to a simple high-vacuum-proofed volume of similar size. The response time was strongly dependent on the conditioning history of the cell, but even by baking, purging, and evacuating the cell over
- 200 few days, the pump-down time of the cell after filling with a sample gas took at least 20 minutes. Hence, we concluded that these characteristics were caused by adsorption processes on the cell inner surfaces and by internally closed volumes acting as "gas buffers". The efforts of trying Trying to fix these issues by coating the surfaces and modifying the constructional design of this cell appeared to be significant and, therefore, we decided to develop a new cellwhile considering all the relevant requirements mentioned above very challenging. Therefore, we decided for the development of a custom-made cell, taking into
- 205 <u>consideration all of the above requirements</u> in its design.

The basic design difference of our cell with respect to the AMAC-36 is the cell-body milled from solid stainless steel, which allows to shape the cell inner surface as a cuboid that matches the envelope of the optical pattern of the laser beam between the two astigmatic mirrors. This design approach leads to a 30 % reduction of the inner volume (to $166 \pm 5 \text{ cm}^3$) compared to the elassical cylindrical design a simple cylindrical geometry and thus increases the pressure of the air sample,

- 210 which is crucial to reach the targeted precision. A further significant benefit of the single-piece cell body is the possibility to manufacture most of the mechanics, required for mirror mounting and aligning, out of the same piece. This allows minimizing manufacturing tolerances and reducing the degrees of freedom for mirror mounting to axial shift and rotation of only-the back mirror. Furthermore Thus, this concept simplifies the inner mechanics and helps in minimizing allows for a simpler alignment mechanism, and hence it also minimizes the dead volume behind the rear-mirror that would be required otherwise.
- 215 Beside the cell-body, the astigmatic mirrors were also reconsidered. The calculation of the geometry of the astigmatic mirror pair is based on the paraxial matrix approach (McManus et al., 1995; McManus, 2007). In general, for a given mirror geometry, there is a large number of possible reflection patterns supported for varying mirror distances and tilt angles. For the search of suitable mirror geometries, we set the following boundary conditions: i) a low volume for the targeted 30 m OPL, and ii) a reflection pattern that generates a minimum of optical fringes, or fringes with frequencies that substantially differ from the
- absorption line widths (about 100 MHz). The first condition is well accomplished met by a base length of 20 cm and mirror



Figure 3. The low-volume and high-vacuum-sealed optical MPC developed and manufactured for the spectrometer. Left: Photograph of the multipass absorption cell with its entry window and the gas inlet in the foreground. The cell inner body along the optical axis is shaped as a cuboid that matches the envelope of the optical pattern of the laser beam between the two astigmatic mirrors. This design approach leads to a 30 % reduction of the inner volume compared to a simple cylindrical/rectangular case. Right-top: Photograph of the custom-made astigmatic mirror with the entry-hole in the center. The mirror body design allows for a direct and leak-tight attachment to the cell thereby minimizing the dead volume. Right-bottom: Reflection pattern (red dots) on the two mirrors as used in the current configuration. The blue and green dots represent the first and last reflection, respectively.

diameters of 4 cm, i. e. for parameters very similar to the design of the commercial AMAC-36. For the second aspect, we first generated a pattern map (McManus et al., 2011) with all possible combinations of mirror curvatures and tilt angle, and then calculated for individual patterns the spatial separation of each reflection spot with respect to its neighbors, and searched for candidates with a high separation level. The expected interference frequencies were derived based on the optical path difference of the neighboring spots. Apart from the lowest possible overlap of the individual reflection spots, we also took into account the optical path difference is comparable to the width of the absorption line. Overlaps of the beam spots with small pass number (e.g. 4 and 6) differences are especially problematic. Searching for patterns that fulfil these criteria are expected to result in reduced optical fringe level and have less impact on the absorption line retrieval. In consideration of all these

diamond turning and post polishing a NiP coated aluminum substrate (LT Ultra-Precision Technology, Germany). Finally, a



Figure 4. Schematic of the electronics setup. The core of the system is a system-on-chip (SoC) embedding a dual-core ARM processor and a FPGA, which triggers the laser driver, reads the ADCs and processes the detector signals in real-time. All processes are synchronized using the same clock generator. The hardware internal communication is based on the Inter-Integrated Circuit (I^2C) protocol. The CPU communicates with the host PC and drives other hardware components, which are less critical with respect to the timing.

broadband high-reflectivity coating (Pleiger Laseroptik, Germany) was applied to achieve 99.0% approx. 99% reflectivity for both selected IR-spectral ranges and 98.0% about 98% for the visible range. The exact optical path length (34.134 \pm 0.003 m) was measured by coupling in a commercial laser distance meter (Disto D510, Leica Geosystems, Switzerland). The highvacuum-proofed construction assures very low leak-rates (<1 × 10⁻⁷ mbar Ls⁻¹) below 1 × 10⁻⁷ mbar Ls⁻¹ and fast pump down times (from 5 mbar to 0.01 mbar in 90 s). This is a prerequisite for fast change-over rapid switching between sample and standard which contributes to a high accuracy in applications with small, discrete samples (see Sect. 3) such as those derived from ice cores.

2.2 Hardware design and data processing

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- Our laser driving and data processing electronics approach are described in detail elsewhere (Liu et al., 2018; Tuzson et al., 2020) and only a brief summary is given here. The two QCLs are driven in intermittent continuous wave (ICW) mode with time-division multiplexed timing (Fischer et al., 2014). Applying By applying the current pulses, the laser emission frequency is rapidly tuned, allowing for complete spectral scans within 75 µs. The tuning-rate is transformed into a linearized frequency scale by using the transmission spectrum of a 2-inch solid Germanium etalon, which is mounted on a custom-made flip-mount.
- 245 Repeated measurements indicate that the QCL tuning characteristics are highly stable over time and new characterizations are only needed after major interventions into on the system.

Hardware control and data acquisition electronics deployed here are similar to those of Liu et al. (2018). The main difference is that <u>here</u> we use a more powerful programmable board (Alpha250, Koheron, France), built around a field-programmable gate array (FPGA), which features faster sampling rate (250 MSs^{-1}) and a higher bandwidth (100 MHz) analog front-end with dual-

250 channel 14-bit ADCs and 16-bit DACs. This upgrade was necessary because of the required higher spectral resolution (narrow line widths due to low-pressure samples) and the dual-path configuration resulting in two simultaneous inputs to the ADC (see Fig. 4). The FPGA firmware (VHDL-Code) and the Linux service routines (C-Code) were custom developed. The FPGA contains a state-machine that is clocked eight times slower than the sample clock, which makes routing less critical, i.e. larger



Figure 5. Gas handling system primarily used to characterize and calibrate the QCLAS instrument (schematically indicated by the gray rectangle), but also to introduce small air samples trapped in dip tubes that contain air extracted from ice core samples. The gas handling system is made out of ultra-high vacuum (UHV) stainless steel tubing and uses exclusively VCR- and KF-seals downstream of the critical orifice. The majority of the valves are pneumatically actuated valves (Fujikin Inc., Japan). For the flow-through measurements, a bypass with a metering valve (not shown) was used to reduce the flow.

data path delays are tolerated. For higher flexibility in data acquisition, several user-defined time-windows within a spectral scan are supported. The summation of consecutive spectra is implemented with digital signal processors (DSP) and dual port block random access memory (BRAM). The spectra are then transferred from the programming logic via direct memory access (DMA) into the DDR-RAM of the processing unit. These data <u>can either be are then</u> sent to an external computer via a TCP/IP-interface or stored on a flash memory for post-processing.

For the spectral analysis, we used the averaged data of 5000 spectra corresponding to 1 Hz time resolution. In total, five
acquisition windows were defined over the two laser pulses. One data acquisition window is used to record the detector signal while the lasers are not turned on yet. This signal is used to normalize the follow-up spectra that are collected in the other four windows within the laser scan. The concentrations of the individual species are retrieved in real-time by fitting a Voigt function to the measured spectra using the Levenberg-Marquardt least-squares algorithm implemented in LabVIEW (National Instruments, USA). The spectral line intensity and the broadening parameters are taken from the HITRAN2016 database
(Gordon et al., 2017), whereas the gas pressure and temperature are measured and their values are used in the fitting algorithm to calculate the Doppler- and Lorentzian-widths and determine the number density of the target molecules. The corresponding transmission spectra with the associated fitted curves using Voigt profiles are shown in Fig. 2.

2.3 Gas handling hardware

A fully automated gas handling system has been built around the spectrometer as depicted in Fig. 5. The system is equipped with two pumps (turbo-molecular pump station and diaphragm pump) used to pull reference gases from the cylinders through parts of the system at a steady flow, independently of the measurement cycle, or to evacuate the MPC and the manifold-line between individual discrete samples. A multi-port selector (6-port, Vici Valco Instruments Inc., Switzerland) with individual vents allows switching between the standard gas cylinders while maintaining an uninterrupted gas flow. After the multi-port selector, the standard gas is pulled through a flow restriction (critical orifice), where the pressure drops from about 2 bar absolute to the

- 275 mbar-level. The critical orifice size $(20 \,\mu\text{m})$ as well as the output pressure of the regulators were all carefully selected to avoid isotopic fractionation as the gases flow through the system. A series of experiments was conducted in flow-through and static regime to investigate potential fractionation effects due to flow-restriction elements such as critical orifice and the optional metering valve used in the flow-through mode. Their effect was found to be lower than our detection limit. With this setup it is possible to operate the instrument both in flow through or in batch mode for discrete samples. In the latter, the evacuated
- 280 MPC is filled to any target pressure between 2.0 and 10.5 mbar with an uncertainty of ±0.04 mbar. For this, a pressure sensor (CMR 363, Pfeiffer Vacuum, Switzerland) monitors the sample pressure in the MPC at 10 Hz and its output signal is used to control the pneumatic valves and decouple the cell when the preset pressure is achieved.

2.4 Custom-made standard gases

Direct absorption laser spectroscopy establishes a well-defined relation between the unknown amount fraction and the measured 285 absorbance. This relation only contains directly measurable physical quantities (temperature, pressure, optical path length, line amplitude) and molecular properties, and thus it makes the technique - in terms of metrology - a calibration-free method to determine the amount fraction of a trace gas (e.g. Buchholz et al., 2014). However, as any "real" system, this approach is also affected by <u>e.g.</u> for example detector non-linearity, drifts, optical fringes or general instrumental response that may change over time. The relevance of these effects is gaining significance as the requirements regarding instrument performance become more stringent, which is especially pronounced for measurements of stable isotope ratios. Relatively stable and predictable 290 instrument-related artifacts can be accounted for by a well-designed calibration scheme, which may also provide traceability to SI-units or an established calibration scale. A widely-used approach is multi-dimensional bracketing with reference gases of known isotopic composition. This targets the most critical dependencies and seeks to link links the measured spectroscopic values to an international scale in a range that covers (or even goes beyond) the expected variations occurring in the samples. 295 Relying on our previous experience in high-accuracy, traceable, long-term, and robust calibration of laser spectrometers for isotope ratio measurements (see e.g. Tuzson et al., 2011; Sturm et al., 2013), we adopted here the strategy of delta-based calibration. For this, we prepared a set of calibration gases with specific mixtures. The aim was to realize 2-dimensional a two-dimensional bracketing for two major goals: i) reliably link the spectrally-derived isotope ratios to the internationally accepted Vienna Pee Dee PeeDee Belemnite (VPDB) scale, and ii) account for the dependency of the retrieved $\delta^{13}C(CO_2)$ 300 values on the CO_2 concentration (Griffith, 2018). In addition, the calibration gases were designed to also provide bracketing of the other two trace gases (N_2O and CH_4). As a result, five standards were prepared (see Table 2), two pairs each having

almost identical δ¹³C(CO₂) (values fixed at <u>3.54% and 10%, respectively 3.7% and 10%</u>), but different CO₂ concentrations covering pre-industrial/glacial-interglacial atmospheric composition (160 ppm and 350 ppm). The fifth standard gas was prepared in such a way that it falls in the middle of the corner values for both δ¹³C(CO₂) and CO₂ concentration, as indicated in Fig. 6. Here, the concentrations of N₂O and CH₄ (Table ??) are indicated by colors (red, green, yellow) that qualitatively reflect the respective trace-gas content (high, medium, and low).

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Table 2. List of custom-made standard gases produced for the calibration of the QCLAS. The concentrations and isotope ratio values cover the range of expected variations found in ancient air samples from ice cores. The standard #2 is only matrix air that was used to generate the various standard mixtures. The uncertainty of the values are given in parentheses.

Cylinder	CO_2	CH_4	N_2O	$\delta^{13}C(CO_2)$
#	(ppm)	(ppb)	(ppb)	(%0)
1.	248.8-248.803 (0.01)	528.6 528.576 (0.05)	242.0 241.987 (0.250)	- <u>6.64</u> - <u>6.639</u> (0.037)
2.	0.2 0.201 (0.01)	0.1-0.121 (0.04)	172.7 - <u>172.692</u> (0.100)	n.a.
3.	157.7 - 157.709(0.02)	331.2 331.178 (0.04)	189.2 - <u>189.190</u> (0.310)	-3.72 -3.722 (0.015)
4.	167.0 - <u>167.044</u> (0.02)	811.0-810.950 (0.03)	340.4-340.387 (0.020)	-9.88 -9.880 (0.017)
5.	345.5 - <u>345.514</u> (0.03)	779.8 -779.778 (0.14)	325.7 - <u>325.678</u> (0.040)	-3.70 -3.697 (0.023)
6.	239.2 239.213 (0.03)	527.2 527.185 (0.08)	236.4 <u>236.351</u> (0.280)	-6.666.659 (0.020)
7.	341.8 <u>341.820</u> (0.05)	339.2 339.236 (0.07)	167.4 - <u>167.381</u> (0.330)	-10.07 - <u>10.074</u> (0.014)

The production of standard gases involved two main steps: (i) gravimetric production of approximate mixtures, i.e. within 10 % of the target, and (ii) subsequent quantification of these mixtures by established, traceable methods. For the first step, the approximate mixtures were realized by sequentially freezing out the targeted pure greenhouse gases in cylinders, followed by

- 310 dilution with greenhouse gas-free atmospheric air. The procedure in detail was: i) evacuate a 50 L aluminum gas cylinder, ii) place the cylinder in a liquid nitrogen bath, iii) cryogenically collect pure CO_2 (with one or two different isotopic ratios), CH_4 and N_2O from gas cylinders, iv) cryogenically collect matrix air using a modified lab-internal-zero-air generator that provided (almost) greenhouse gas-free atmospheric air with unchanged $N_2/O_2/Ar$ ratio. This is an important aspect to avoid any potential bias caused by uncertainties in pressure broadening effects of these species (e.g. Nara et al., 2012). One important advantage
- of this cryogenic trapping is that it enables the production of large volumes (6500 L STP) of standard gases(see Table ??), because the gas cylinders can be filled up to their maximum filling pressure limit (200 bar). This permits the production of a set of cylinders with standard gases that will last for many years. In a second-final step, the cylinders were analyzed against NOAA/ESRL standards at the World Calibration Centre (WCC) at Empa for CO₂, CH₄ (CRDS, G1301, Picarro Inc., USA) and N₂O (QC-TILDAS, Aerodyne Research Inc., USA) concentrations several times over the following weeks to investigate
- 320 potential drift effects drifts that may appear due to the cryogenic filling. The results show that all cylinders provide stable concentrations after less than two weeks. The $\delta^{13}C(CO_2)$ isotope ratios were analyzed at the University of Bern (Switzerland) against JRAS-06 reference gases (Wendeberg et al., 2013; Van Der Laan-Luijkx et al., 2013).



Figure 6. Range of CO_2 concentration and $\delta^{13}C(CO_2)$ isotope ratio-spanned by our custom-made standard gases. The CH_4 and N_2O content is indicated by the different colors: red, green and yellow representing high-, medium-, and low-concentrations, respectively (see also Table $\frac{22}{2}$).

3 Performance and Calibration

3.1 Precision and stability in flow-through mode

- The precision and long-term stability of the system is derived with a reference gas continuously flowing through the instrument. A standard gas (#6 in Table 2) was continuously supplied to the MPC at a constant pressure of 5 mbar (corresponding to a cell volume of about 1 ml STP) and a flow of $7 \,\mathrm{mL\,min^{-1}}$ over twelve hours. In this regime, potential artefacts due to sorption effects on surfaces are mostly negligible.
- Figure 7 shows the results of an Allan-Werle variance analysis (Werle, 2011) of the time-series for all four parameters. The data follow a white noise behavior for about 100 s, except for CO_2 , which flattens out already after 10 s, and then stays at low values until at least 400 s before drifts begin dominating the measurements. This information is crucial for an accurate calibration, because it determines the longest time available for the analytical a measurement cycle, i.e. the time interval within which a sample-standard measurement sequence of a discrete air-sample and a subsequent, pressure-adjusted standard-sample has to be performed. Our setup-analyzed. Currently, our custom-made MPC requires about 300 s to completely evacuate the
- 335 MPC and subsequently fill it with a standard be completely evacuated and subsequently filled with another gas (see Sect. 3.2). This relatively rapid exchange time is due to the improved leak-tightness, surface inertness as well as lower dead-volumes, and it is thus well matched with the above constraint. This illustrates the importance of the improved leak-tightness and minimal surface interactions of the custom-made MPC well within the constraints defined by the Allan variance minimum. Follow-up experiments using static (batch-mode) configuration led to comparable precision levels to that of flow-through measurements.
- 340 However, when performing Allan-Werle deviation analyses for discrete samples, the maximum duration of the analyses was limited to half an hour to avoid any noticeable contribution from surface effects related artifacts.

In parallel to the measurements in the MPC, data from the reference cell were also recorded. For CO_2 , CH_4 and N_2O , only a marginal correlation between the two time-series was found. Thus, normalization with the reference cell did not improve the performance. The situation is slightly different for $\delta^{13}C(CO_2)$, where the Allan-Werle deviation minimum could be improved

towards longer integration times (>100 s) by using the reference cell records to apply a drift correction in the form of a simple subtraction of the reference cell mean-normalized data from the MPC data. Therefore, the This different behaviour of $\delta^{13}C(CO_2)$ can be understood by considering the facts that i) this quantity is a ratio between two measured quantities of ${}^{13}CO_2$ and ${}^{12}CO_2$, and therefore, the random errors of these quantities sum up in the ratio, but correlated drifts are eliminated, and ii) $\delta^{13}C(CO_2)$ is temperature sensitive as discussed in Sect. 2 in the context of line selection. The reference cell data canmainly,

and optionally to slightly (optionally) to further improve the precision of $\delta^{13}C(CO_2)$.

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Overall, the precision targets for all the four parameters (see Sect. 2) are reached parameters are reached in the flow-through mode within 10 s integration. The Integrating over 100 s, the instrument achieves a precision of 0.4 ppb, 0.1 ppb, $\frac{6 \text{ ppb}}{0.006 \text{ ppm}}$, and 0.02 ‰ for CH₄, N₂O, CO₂, and δ^{13} C(CO₂), respectively, when integrating over 100 s.

therefore, be used for monitoring purposes, i.e. to efficiently flag out periods with daily variations that eventually can happen



Figure 7. Allan-Werle deviation plot for all observed parameters in a flow-through experiment using the standard gas #6. For $\delta^{13}C(CO_2)$, two situations are shown: i) no drift correction (light green) and ii) applying a drift correction based on the reference cell (dark green). While in the case of isotope ratio values a slight further improvement towards longer integration time can be observed, the concentrations are only marginally influenced (not shown). The optimal integration time is indicated by the gray area.

355 3.2 Repeatability of discrete 1 mL STP samples

The final application of the instrument is the accurate (SI-traceable) measurement of discrete, very small 1 mL air samples that need to be measured in batch mode due to their low volume. As mentioned above, the Allan-Werle deviation analysis indicates that for highest accuracy the sample-standard measurement should take place within 400 s. The gas inlet system (see Fig. 5) was developed to allow the corresponding rapid switching between gases, while maintaining a precise pressure matching within

360 ± 0.04 mbar. For the removal of the gas from the MPC we also consider the specific ice core application, which foresees the option to cryogenically recollect the gas sample after the spectroscopic measurement in a cold finger for further MS analysis. Therefore, the sample gas is not simply flushed out of the cell with the stream of the following standard gas, but rather we evacuate the cell using the turbo-molecular pump to levels near to the detection limit of the cell pressure gauge (10^{-3} mbar), which is similar to the case of a cryogenic recollection. The total delay time between the sample and the standard is around 365 270 s, which is acceptable regarding the stability of the system (Fig. 7) and our precision targets (Sect. 2).

To evaluate the repeatability of discrete sample measurements of 1 ml STP volume 1 ml sample measurements, the following procedure is used: First, a dip tube is filled with about 1 ml STP of a standard gas, and then expanded into the evacuated MPC and treated as the 'sample' in the evaluation procedure. Second, for the 'standard' measurement, the MPC is evacuated again, and the same standard gas is introduced directly, i.e. not via dip tube, until reaching the same cell pressure. This sequence takes 10 min and is repeated several times (50×) and consecutively applied for low-, mid- and high-concentration trace gas standards (see as indicated in Fig. 6). To minimize potential biases originating from long-term optical drifts, we recorded spectra with evacuated cell ('zero trace') at the beginning of each sample-standard pair, which were then subtracted from consecutive spectra. This strategy efficiently removes residual structures in the spectrum that can slowly vary with time and influence the spectral fit.

- The result of this experiment is summarized in Fig. 8. Here, the averages of individual sample-standard pairs recorded over 24 h are displayed along with their associated histograms showing the distribution of the respective values. We found a 1σ - 1σ standard deviation of 2.2 ppb, 0.7 ppb1 ppb, 0.03 ppm and 0.04‰ for CH₄, N₂O, CO₂ and $\delta^{13}C(CO_2)$, respectively. These values are higher by a factor 2 –for $\delta^{13}C(CO_2)$, 5 –for CH₄ and CO₂, and 10 for N₂O than those derived from the Allan-Werle deviation analysis of the flow-through measurements (see Fig. 7). Although this trend is expected, the results
- 380 indicate This indicates that significant uncertainty is introduced by the evacuation and the gas flows gas handling process (e.g. temperature, mechanical stress), as well as by the gas handling process (e. g. adsorptionpressure and temperature induced instabilities during evacuation/desorption). Overall, the filling process, and/or adsorption/desorption effects along the sampling system). Although, individual or discrete gas samples can be measured with a precision as determined by the Allan-Werle deviation analysis, additional artifacts/biases, mainly originating from gas handling, will affect the repeatability and accuracy
- 385 of the measurements when switching between sample gases collected in dip-tubes. Thus, the overall accuracy is not limited by the purely spectroscopic performance, indicating that further improvements may be possible by optimizing the sample handling. Nevertheless, the targets Fig. 8 clearly demonstrates that with our cyclic measurement approach, i.e. quickly alternating between dip-tube sample and reference gas measurement, the instrumental drifts can be accounted for and thus, their effect can



Figure 8. Repeatability of discrete 1 mL sample measurements (mean value subtracted) of 1 ml STP volume with associated histograms showing the indicating a normal distribution of the values. These indicate normally distributed data. The bins were chosen as follows: 0.02 for , 0.01 for , 1 for , and 0.5 for .

be minimized even for longer periods of time, i.e. over 24 h. Thus, the target performances are achieved for all compounds,
 and this spectroscopic performance is maintained at least over 24 h of continuous operation.

3.3 Calibration characteristics of discrete 1 mL STP samples

In this section, we investigate the characteristics of the instrument response using the custom-made and externally calibrated standard gases (Table 2) and derive corresponding calibration functions for discrete 1 ml STP air samples. We use the same measurement procedure as described in sectSect. 3.2. The only difference is that the sample gas is not transferred via the dip tube, but introduced directly into the MPC in the same way as the standard gas. In other words, the sample-standard pair are basically identical measurements with the same gas at the same pressure (5 mbar). Thus, half of the data were used to monitor potential drifts in the spectrometer response, while the other half served to retrieve the target parameters. First, the values of

each category ('anchor' and 'sample') are averaged for 100 s and then, whenever long-term drifts are larger than $\frac{3\sigma}{3\sigma} \frac{3\sigma}{3\sigma}$ of the

- 400 uncertainty of individual values, the drifts are taken into account by applying a smoothing-spline (Igor Pro v8, Wavemetrics Inc., USA) over all 'anchor' values considering their individual standard deviation as weighing factor for the spline, and setting the smoothing factor to unity(Igor Pro v8, Wavemetrics Inc., USA). After drift correction, the ten individual 'sample' values of each standard are averaged and plotted against their reference value, as shown in Fig. 9. Thereby, we found that a linear calibration function describes properly the instrument response for all three trace gas concentrations. For Note that the values
- 405 reported for the laser spectrometer are purely based on spectroscopic (HITRAN) and physical parameters (*P*, *T*, and *OPL*) without any additional calibration. In the case of the $\delta^{13}C(CO_2)$, the calibration following additional approach was used: the CO₂ isotope ratio was re-scaled to the VPDB-scale using an isotope ratio value of $R_s = 0.0111802$ (Werner and Brand, 2001). To make the range of measured- and the reference δ -values comparable, an offset of 9% was added to the measured values. This offset most likely originates from the uncertainty of line strength of the CO₂ isotopologues, but fitting errors (e.g. absorption
- 410 profile mismatch) or other spectral artefacts can also not be excluded. This offset can optionally be included in the calibration function, i.e. in d_0 in Eq. 2.

The calibration of $\delta^{13}C(CO_2)$ is a two-step process as its concentration dependence should must also be considered (see e.g. Tuzson et al., 2008). This concentration dependence of $\delta^{13}C(CO_2)$ is determined based on the measurements of standard gases #3 and #5 (see Table ???2). As both standard gases have the same CO_2 isotopic composition, the apparent difference

415 observed in the spectroscopically-derived isotope ratios is assumed to be entirely due to attributed to the difference in the CO_2 concentration. This two-point calibration, which was found to be about 0.005% ppm⁻¹, is then applied to all the other $\delta^{13}C(CO_2)$ values obtained for the different standard gases. Thus, the specific calibration functions of all four parameters are defined as follows:

$$[\mathbf{X}]_{cal} = a_0 + a_1 \cdot [\mathbf{X}]_{meas} \tag{1}$$

420 $\delta^{13}C_{cal} = d_0 + d_1 \cdot \delta^{13}C_{meas} + d_2 \cdot [CO_2]_{meas}$ (2)

where, the subscripts 'meas' and 'cal' denote the measured and the calibrated values, [X] stands for CO_2 , CH_4 and N_2O concentrations, while a_i , and d_i represent the fit coefficients. Figure 9 shows the calibration functions and the resulting residuals for all four parameters.

Although, the spectroscopically-retrieved concentrations show a good linear correlation with the reference values, a systematic underestimation is observed, which in case of CO_2 is 5%. This is slightly more than expected based on propagating errors in 2.7%. However, this is well within the total uncertainty of spectral (e.g. line intensitystrength) and physical (pressure, temperature, and OPL) parameters. As all species show similar characteristics, it is most likely an indication for a common underlying bias. There are mainly two Additionally, there are two other effects that could contribute to such a the observed bias: i) the Voigt profile used to fit the absorption lines tends to underestimate the effective absorption line areas especially at

430 low pressure, and ii) the absorption lines might be slightly saturated by the incident laser optical power. Underestimation by the Voigt profile is well documented , however and the literature suggests a bias between 1-2% for our working pressure (Bui et al., 2014; Lisak et al., 2015)and thus only partly explains our observation. There. Using more sophisticated line profiles, such as the Hartmann-Tran profile (HTP) (Ngo et al.) in the spectral evaluation has the potential to reduce the observed mismatch (see the characteristic residual structure in Fig. 2), but most likely will not affect the precision or its impact will only be marginal. One

- 435 key issue is, however, that the additional line parameters required for the HTP line shape model are not available. Nevertheless, the raw spectra have been recorded and they can be post-processed at a later time. Furthermore, there is a strong evidence that optical saturation plays a significant rolehas a bias contribution as well, despite the implemented intensity reduction scheme (see as discussed in Sect. 2.1). This is supported by the observation that increasing cell pressure leads to an increasing slope of the calibration functions a decreasing bias in the retrieved concentrations (see Fig. 10), which is in line with the expected
- 440 behavior of optical saturation; higher gas pressure means higher collision rate, which causes faster relaxation of the states and ultimately reduces the number of molecules that are in the excited state. Nevertheless, the Based on these experimental data and further investigations of absorption signals at high- and low laser intensities, we estimate, assuming the inhomogeneous broadening regime, the saturation coefficient *s* to about 0.014, which correspond to a saturation effect of 0.7%. In any case, the systematic error caused by this effect is included in the calibration process, because the main factors that have an impact on
- 445 saturation are kept constant, e.g. temperature, pressure, laser intensity or gas matrix. To verify this assumption, we determined the instrument response to our standards in five sets of experiments, with about two-week-at least two-weeks or more time lag between each. Each set of experiments involved repeated evacuation/filling cycles of the MPC, and every standard gas was measured twenty times in a scheme as described above. We found excellent agreement across all these measurements, which demonstrates the constant analytical performance of the instrument.
- It should be noted that the amount of gas resulting from ice core samples, and thus the sample pressure in the MPC, may slightly fluctuate, depending on the air content of the sublimated ice core. At the high level of required accuracy, this may be a critical parameter. Preliminary tests with the sampling and calibration procedure described here above were performed to investigate the influence of gas pressure variation on the spectroscopically-retrieved values. For this, we repeated the same procedure that was used for the calibration measurements with the only difference this time being that that this time
- 455 the 'sample' measurements were done at various pressures covering the range between 2 and 10.5 mbar. Figure 10 shows the representative results for one standard gas. This indicates that basically every target parameter is affected by changing cell pressure. Whilst, , despite the fact that the gas pressure values are used in the fitting algorithm to calculate the corresponding Lorentzian width contributions to the absorption line and also in the determination of the number density of the target species based on the ideal gas law. Whilst for the CH₄ and N₂O concentration retrieval the influence of pressure is
- 460 about $0.76(19)0.76 \pm 0.19$ ppb mbar⁻¹ and $0.31(3)0.31 \pm 0.03$ ppb mbar⁻¹, respectively, the $\delta^{13}C(CO_2)$ and the CO₂ concentration values show a strong and non-linear dependence, especially towards lower cell pressures (<5 mbar). Obviously, this effect can significantly the pressure dependence can deteriorate the spectrometer accuracy if it is not taken into account properly. Therefore, the pressure Considering a narrow pressure region around 5 mbar, the dependency of $\delta^{13}C(CO_2)$ on pressure is about 0.81% mbar⁻¹. Thus, in order to achieve 0.04% precision on the isotope ratio, an accuracy of 0.05 mbar on the
- 465 pressure measurement is needed. Our pressure sensor (CMR 363, Pfeiffer Vacuum, Switzerland) has a stated accuracy of 0.2 % of the measured value, i.e., an uncertainty of 0.01 mbar for the 5 mbar sample pressure. As mentioned above (see sect.2.3), the pressure matching between consecutive batch samples is better than 0.04 mbar. Based on these findings, the pressure either has



Figure 9. Calibration functions and corresponding residuals from the fit of all four analyzed parameters for a sample with of 1 ml STP volume, corresponding to 5 mbar pressure in the MPC. The dashed gray lines indicate the 1:1 correlation as reference.

to be actively controlled or and accurately adjusted or it has to be considered in the data retrieval. In the former case, an additional buffer volume with flexible bellows can be added to the gas-handling system to precisely adjust match the cell pressure
to a preset value for any ice core sample. Otherwise, the calibration functions have to be known for each pressure value. This is feasible because the pressure dependency of the target parameters have smooth characteristics and can be described by simple analytical functions (linear, polynomial or exponential). These relations hold also for the calibration function coefficients, which can then include a pressure-dependence correction term. Although, it involves a slightly higher complexity, such an approach was tested successfully using interpolated calibration function coefficients for a randomly taken pressure value. Nev-

475 ertheless, the final accuracy of the measurement will sensitively depend on the uncertainty from reflect the uncertainty of the extrapolation between the used individual calibration functions. Therefore, the best practice is still to establish an experimental



Figure 10. Pressure dependence of the target parameters. The same standard gas is used alternately as 'anchor' (diamond) and 'sample' (circle). The gas pressure for the 'anchor' is kept at 5 mbar, while the pressure of the 'sample' is gradually changed between 2 and 10 mbar (top plot). The markers represent the mean value of the measurements taken at each pressure value over 70 s. The overall sequence is repeated three times for the same standard gas and then consecutively applied to the other five standards. The instrumental response remained stable during the entire measurement time (>25 h).

solution, which maintains the cell pressure of the different samples and standard gases identical, possibly at values $\geq 5 \text{ mbar}$. Furthermore, it is advisable to use standard gases that are similar to the unknown sample in both concentration and isotopic composition. Fulfilling these two conditions, the spectrometer accuracy would approach its precision level. For the ice core

480 application, a more detailed characterization and validation of the pressure-dependent calibration parameters in the desired pressure range a smaller pressure range around the pressure span expected from an ice core sample is required. Here, we provided the instrument behavior over the whole possible operation range, which can build is the basis for future work with this spectrometer in its final configuration including the ice core extraction system. Furthermore, it is advisable to use standard gases that are similar to the unknown sample in both concentration and isotopic composition. Last but not least, applying a more sophisticated line shape model in the fitting algorithm (see discussion in Sect. 3) has also the potential to minimize the observed pressure dependence by better matching the measured absorption signal.

Finally, a significant advantage of laser spectroscopy over - for instance - mass spectrometry is that the absorption lines are molecule-specific and interferences between different gases are unlikely. In the case of ice core analyses, in particular, the use of organic drill fluids may, however, lead to contamination with potentially absorbing compounds. Therefore, we tested for spectral interferences with the drill fluid ESTISOL[™] 140, which is to be used in Antarctica within the Beyond EPICA ice core project. This substance was introduced into the multipass cell in trace quantities that are expected to be representative for the ice core samples. This led to no alterations in the observed spectrum within the selected spectral window, which is not surprising, because such large organic compounds usually have very broad absorption features and tend to be localized to

495 4 Conclusions

frequencies typical for functional groups.

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A dual-QCL direct absorption spectrometer has been developed for the challenging measurements of small (1 ml STP) ice core samples. The stringent requirements in precision and accuracy were met by the design, development, and implementation of the following key elements: i) a new low-volume multipass absorption cell was designed with a special focus on minimizing contamination effects (e.g. surface adsorption, outgassing, leak-rate), improving optical performance (low fringe level) and robustness against mechanical and thermal variations; ii) a custom-made low-noise/low-drift laser driving electronics stabilized by a thermoelectrically cooled water-loop; iii) a fast dual-channel real-time data acquisition system based on FPGA SoC; and iv) a dedicated system-tailored and automated gas handling manifold to manipulate low-volume samples.

Flow-through experiments demonstrate an analytical precision $\frac{0.6 \text{ ppb}}{(1 \sigma)} \frac{1 \sigma}{0.006 \text{ ppm}}$ for CO₂, 0.02% for δ^{13} C(CO₂), 0.4 ppb for CH₄ and 0.1 ppb for N₂O obtained after an integration time of 100 s. Sample-standard repeatabilities (1 σ) of dis-

- 505 crete samples of 1 ml STP amount to of 0.03 ppm for CO_2 , 0.04% for $\delta^{13}C(CO_2)$, 2.2 ppb for CH_4 and 1 ppb for N_2O and meet or even exceed our ice core precision targets. Furthermore, calibration curves have been determined and verified in repeated measurements over a time span of several months, and it was found that the instrument can provide provides calibrated values with uncertainties similar to the repeatabilities. Thus, the spectrometer is capable of simultaneously and accurately analyzing discrete air samples of 1 mL STP volume for their CO_2 , $\delta^{13}C(CO_2)$, CH_4 and N_2O compositioneven at 1–2 ml
- 510 STP volume as expected from future ice core samples. Further improvements of the instrument performance can be expected from the implementation of a more sophisticated line profile beyond the Voigt-model in the spectral fitting algorithm. Thereby, a more accurate concentration retrieval and potentially a less eminent pressure dependence may be achieved, which would alleviate the pressure on careful calibration as used in this study. Finally, it was verified that the laser spectroscopic approach is immune against potential contamination compounds such as drilling fluids. Being a non-invasive analytical tool, it also
- 515 allows to reuse the measured sample for further analysis. Therefore, this new instrument is an ideal tool for future technique, it allows reusing the precious samples for further ice core analyses after cryogenic recollection from the multipass cell. Overall, this approach opens many options for further analytical improvements and technological developments in ice core researchas targeted by the planned drilling of a 1.5 Myr old ice core from Antarctica.

Data availability. The data used in this manuscript are available from the corresponding author upon request.

520 *Author contributions.* B.B. designed and developed the instrument under the guidance of B.T. and with input by L.E. and H.F., while L.M., D.B., and J.S. realized the gas handling system. B.B., L.M., D.B., and J.S. performed the experiments and evaluated the data. P.S. designed and developed the electronics hardware. A.K. developed and implemented FPGA and DAQ functionalities. H.L. developed the spectral analysis and hardware control software. H.F together with L.E. and B.T. designed the research, managed and supervised the project, and discussed the results. B.B. and B.T. prepared the manuscript with contributions from all authors.

525 Competing interests. The authors declare that they have no conflict of interest.

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