

19ENV05 STELLAR

(Stable isotope metrology to enable climate action and regulation)

D7

Good practice guide on monitoring stations / gas handling for carbon dioxide and methane isotope analysis, and achieved in-field compatibility between different OIRS and IRMS with a target precision of 0.05 ‰ for $\delta^{13}\text{C}\text{-CO}_2$ and $\delta^{18}\text{O}\text{-CO}_2$

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Table of Contents

Table of Contents	2
1. Target audience	3
2. Introduction	3
3. Planning and setting up field campaigns: OIRS instrument requirements	3
3.1 Evaluating minimal requirements for monitoring stations	3
3.2 Example minimal requirements for different field campaigns/analyzers.....	4
3.2.1 Example 1: NPL Boreas – A sample preconcentration dual laser ($^{13}\text{C}/^{12}\text{C}$ and D/H) spectrometer	4
3.2.2 Example 2: Empa TREX-QCLAS – A sample preconcentration dual laser ($^{13}\text{C}/^{12}\text{C}$ and D/H) spectrometer	4
3.2.3 Example 3: PTB -Two OIRS analyzers for measuring isotopic compositions of CO_2	5
3.3 Suggestions for remote operation and monitoring.....	6
4. Recommendations to evaluate and reduce uncertainty contributions under field conditions.....	6
4.1 Factors that change data quality	7
4.1.1 Temperature changes.....	7
4.1.2 Gas composition changes	7
4.2 How to monitor data quality under field conditions	8
4.3 How to calibrate under field conditions	9
4.3.1 An example calibration setup in the field: The NPL Boreas system	9
4.3.2 Recommendations for calibration gas handling.....	9
5. Exemplary field measurements with OIRS	11
5.1 Comparing temperature stability under field and lab conditions	11
5.2 Source measurements from the atmosphere (UEF)	13
5.3 Ambient CO_2 measurements from atmosphere (VTT)	14
6. Options to quantify OIRS-IRMS in field compatibility	17
6.1 Example 1: Compatibility of analytical techniques for CH_4 isotope measurements	17
6.2 Example 2: OIRS IRMS comparison measurements of isotope ratios	18
i) Measurements at NPL.....	18
ii) Measurements at BCG-IsoLab	20
6.3 Example 3: Comparison measurements of amount fraction.....	20
6. Acknowledgements	22

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1. Target audience

This document addresses NMIs and the end-users who carry out OIRS measurements at monitoring stations. The report includes minimal requirements for field measurements, calibration routines of the instrument and sample handling. The field measurements process and achieved sensitivities are also included. It highlights the steps for remote monitoring and factors to be considered to reduce uncertainties/ calibration routines for on-site measurements. Comparison measurements for OIRS and IRMS are also added.

2. Introduction

The previous guideline reports have covered the application of OIRS for atmospheric measurements, including sample handling protocol, optimized analytical procedures, traceability to the international standards and target uncertainties for both carbon dioxide and methane (Braden-Behrens et al 2023, Rennick et al 2023) while, in this document we focus on field measurements. This document highlights the OIRS instruments used for field measurements, the minimum requirements for operating these instruments, recommendations for reducing measurement uncertainties, and finally some results.

3. Planning and setting up field campaigns: OIRS instrument requirements

3.1 Evaluating minimal requirements for monitoring stations

When planning an OIRS based field campaign, an evaluation of the minimal requirements of the experimental setup can help in achieving a comprehensive dataset and to reduce uncertainties. The minimum requirements will include:

- 1) **Infrastructure requirements**
such as remote-control options, rain protection and stability of the power supply including options to handle differently long power supply failures,
- 2) **Maintenance requirements**
such as replacement of drying material, calibration cylinders or filters
- 3) **Instrumental requirements**
such as required temperature stability, required flow rates and pressures as well as operational ranges (pressure p , temperature T and flow rate Φ)
- 4) **Expected measurement ranges (amount fraction χ and delta value δ), instrument ranges (χ and δ) & detection limits (χ)**
such as expected variability of χ and δ during the experiment and guaranteed specification ranges of the instrument

5) Consumables

such as purging and calibration gases, filters

6) Sample preparation systems

such as dryers and preconcentration setups (see e.g., the setup used by NPL and EMPA, in this report, for dual isotope analysis of CH₄)

7) Auxiliary measurements

such as temperature and humidity sensors or additional CO₂/CH₄/H₂O analysers.

Further information is provided by station specifications of monitoring networks such as ICOS or WMO GAW.

3.2 Example minimal requirements for different field campaigns/analyzers**3.2.1 Example 1: NPL Boreas – A sample preconcentration dual laser (¹³C/¹²C and D/H) spectrometer**

For the Boreas system (NPL design and construction) the following minimal requirements were identified:

- Temperature range 15°C - 25°C, stability better than ±1°C
- Sample gas flow rate 4.5 L/min, pressurized at up to 5000 hPa.
- Carrier gas cylinder of high-purity nitrogen at a total flow rate of up to 1 L/min pressurized up to 5000 hPa
- Maximum consumption 3.2 kW including all vacuum pumps.
- Power connection either multiple 13A sockets for sub-systems or 32A socket for single connection to uninterruptible power supply.

3.2.2 Example 2: Empa TREX-QCLAS – A sample preconcentration dual laser (¹³C/¹²C and D/H) spectrometer**i) TREX (Empa design and construction, see Prokhorov et al. 2022, Eyer et al. 2016):**

- Estimated temperature range: 10-35°C
- Estimated relative humidity: < 90%
- power connection: 230 V AC, 50 Hz
- Expected power consumption: max 1.5 kW at start-up
- Sample gas specifications: flow < 1 L min⁻¹, dehumidified (dew point < 230 K), particle filtered, pressurized 4'000 hPa
- Support gas specifications: high purity nitrogen (99.9999 %), pressurized 3'000 hPa

ii) QCLAS (Aerodyne Research Inc., with T-insulation box):

- Estimated temperature range: 15-25°C (T stability $\pm 2^\circ\text{C}$ or better)
- Estimated relative humidity: < 90%
- power connection: 20/240 V AC, 50/60 Hz
- Expected power consumption: max 1.2 kW at start-up
- Sample gas specifications: particle filtered, non-condensing
- Purge gas specifications: 1 l min⁻¹, low dew point, CO₂ free

Auxiliary instruments to acquire supportive measurements:

- High-precision CH₄ concentration measurement (e.g. Picarro G2401)
- High-precision CH₄ and C₂H₆ concentration (e.g. Aeris CH₄/C₂H₆)
- Meteorological parameters required for data interpretation

3.2.3 Example 3: PTB -Two OIRS analyzers for measuring isotopic compositions of CO₂

At PTB, two different OIRS analyzers are used to measure the ¹³C/¹²C composition of CO₂ in air/N₂. The Delta Ray analyzer (Thermo Scientific) is a laser-based direct absorption spectrometer in the mid infrared, and the Picarro G2201-i is a cavity ringdown spectrometer. The minimal requirements for those analyzers are listed below:

i) Delta Ray (see Thermo Fisher Scientific. 2016)

- temperature range: 10-35°C
- temperature stability: <0.2°C/min
- relative humidity: 10-80% for T<31°C; 10-50% at T=40°C
- power connection: 100–240 V AC, 50/60 Hz
- expected power consumption: app. 220 W at operation (Braden-Behrens et al, 2017); maximum 695 W at startup
- Sampling line: Condensation along the sampling line should be avoided (e.g., by heating at pressure drops) to avoid ¹⁸O exchange between condensed water and CO₂ (see Braden-Behrens et al, 2017).

ii) Picarro G2201i (see Picarro 2016)

- temperature range: +10 to 45°C
- temperature stability: +-0.005°C
- relative humidity: <99%
- power connection: 100–240 V AC, 47/63 Hz
- expected power consumption: <260 VAC (startup), 160 (operation)

3.3 Suggestions for remote operation and monitoring

3.3.1 Remote operation

The instrumentation should be capable of continuous remote operation with minimal user interaction. It is recommended, however, that the site has internet access for remote monitoring. This should comprise alerting, such as emails automatically sent when instrumental parameters exceed pre-set limits, and monitoring, i.e. regular review of data to identify changes such as drift that may need manual intervention.

3.3.2 Multi-stage strategy for power supply failures

A possible multi-stage strategy to deal with power failures could for example differentiate between:

- **short term power loss** that can be dealt with by operating the whole system including pumps by a UPS (based on batteries that supply enough power for the short period)
- **medium term power failure** that allows limited operation of the setup (e.g., running only core elements but shutting down some pumps) for a certain time and allows going back to the full setup if the power failure ends.
- **longer power failure** that required a controlled shutdown of the analyser and all pumps. Depending on the sensitivity of the analyser, one needs to consider if the setup should automatically restart if power comes back or if this is suppressed e.g., by using a zero-voltage switch.

The details and the suitability of such a multi-stage strategy to deal with power supply failures highly depends on the analyser and the infrastructure of the field site. However, we recommend evaluating possible power failures (e.g., by analysing past events at a given field site) and to carefully consider different options for differently long power failures to avoid data loss.

4. Recommendations to evaluate and reduce uncertainty contributions under field conditions

If a calibration based OIRS system is applied under field conditions, there might be uncertainty contributions that are larger than in a controlled lab environment. Those changes could be for example related to more pronounced temperature changes, enhanced vibrations, power failures, or a more variable sample gas composition. Here, we discuss those effects and recommendations to detect and reduce their impact on data quality in detail.

4.1 Factors that change data quality

4.1.1 Temperature changes

Effects of temperature changes on data quality can be related to temperature changes at

- the instrument
- the calibration cylinders
- the gas inlet system

As field conditions typically involve fewer stable temperatures, any uncertainties related to temperature changes might get more pronounced in the field compared to the laboratory.

To minimize those effects, we recommend to:

- Operate the analyser in a temperature-controlled environment (trailer or rack) if feasible.
- Carefully track and analyse temperature fluctuations and plot data together with δ values and amount fractions and instrument (e.g., cell / laser temperature) and additional parameters (e.g., inlet temperature, ambient temperature).
- Avoid condensation along the sample gas line, keep in mind, that pressure increases might induce condensation.
- Store calibration gas cylinders in the air-conditioned trailer if feasible, minimise tube length and use appropriate/tested regulators and tubing materials. Test the tubing for leaks to avoid high consumption.
- Carefully check the sampling line for leakages.

4.1.2 Gas composition changes

- Close-by emission sources (e.g., dairy farming or gas wells) might impose spectral interferences or gas matrix effects depending on the source and analyser type. A first assessment should be done for known co-emitted trace gases (e.g., NH_3 , C_2H_6) by literature or spectral database analysis or checking the instrument spectra for non-target absorbances.
- Rapid changes in amount fractions of CO_2/CH_4 will affect the stability and calibration of the isotope composition measurements. These changes will have the consequence that the optimal integration time is not reached, leading to increased measurement uncertainties. Calibration gases should always bracket the sample measurements, which might be more challenging in the field due to the higher range in amount fractions that are measured.

- **To minimize the effects, we recommend the following:**
If a spectral interference or gas matrix changes are probable, the component should be removed from the sample gas prior to analysis by adsorbents, catalysts, etc. It should be tested, whether the adsorbents, catalyst affects the target gas composition.
- Alternatively, the effect of interferant or gas matrix change on the apparent target gas composition should be characterised to apply a data post-correction. Corrections functions might be more complex depending on target gas concentration or variable in time.

4.2 How to monitor data quality under field conditions

- We recommend analysing the instruments stability under field and lab conditions e.g., by performing an Allan Variance test on a stable gas supply as described in the ‘Good Practice Guide for CO₂ measurements’, Braden-Behrens et al. 2023. Those stability tests should be performed over a sufficiently long period including and excluding the plumbing, while the following practical limitations at remote locations need to be considered: Stability tests and target measurements that exclude the plumbing are useful and important to understand the analysers performance. However, connecting a stable gas source to the sample inlet including the plumbing provides important insights into fractionation effects and leakages along the sample line. For complex setup and high or remote inlets, it might be challenging to implement this after all tubes are installed– in such cases it could be an option to test the inlet before installation.
- Depending on the field site and the flow rate, an Allan variance test with a stable gas cylinder at the applications flow rate over several hours might be challenging. If practical limitations do not allow such a test, it could be an option to assess the stability of analysers (Allan variance) for periods with stable gas composition/no pollution events. Throughout the measurement campaign, we recommend performing target gas measurements at different times of the day (e.g., chose 5 h instead of 6; 11 instead of 12 h or 23 instead of 24 h) to capture changes in instrument performance related to diurnal cycles.
- Another possibility to trace data quality (uncertainty) is to collect flask samples aside OIRS measurements and ship them to an expert laboratory for IRMS analysis (see section 5.1).

4.3 How to calibrate under field conditions

4.3.1 An example calibration setup in the field: The NPL Boreas system

There are two stages to the calibration of the NPL Boreas system for $\delta^{13}\text{C}$ (CH_4) and $\delta^2\text{H}$ (CH_4) isotope ratios: calibrating the spectrometer response to the preconcentrated sample and calibrating for drift or fractionation in the preconcentration process. The spectrometer calibration is performed using two primary reference materials (PRMs) gravimetrically prepared using high-purity methane in a nitrogen matrix at nominal amount fractions around $500 \mu\text{mol mol}^{-1}$ and $625 \mu\text{mol mol}^{-1}$. These are selected to match the matrix of the preconcentrated sample and bracket in total CH_4 amount fraction. This method calibrates instrument response to the $^{12}\text{CH}_4$, $^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$ isotopologues then calculates isotope ratio from these; this is described in [reference D6]]. Calibration of the preconcentrator is performed using a gas cylinder containing compressed whole air following the principle of identical treatment – this standard gas is analysed in the same way as the ambient air sample at regular intervals.

4.3.2 Recommendations for calibration gas handling

Gas handling recommendations for CO_2 measurements have been discussed in detail in the ‘Good Practice Guide for CO_2 measurements’, Braden-Behrens et al 2023. Here we provide a summary of these recommendations, focussing on those that are particularly relevant for field measurements:

- **Operating Conditions (e.g., operating mode, pressure, and flow rate)**
OIRS analysers can be operated in different operating conditions such as static mode or continuous mode at different flow rates (Braden-Behrens et al 2023). In brief, different analysers have different cell volumes and operate at different (sometimes adjustable) pressures. When planning a field campaign and choosing a suitable analyser for a certain experiment, those conditions need to be carefully considered and chosen, as they can influence both: the analysers performance (e.g., stability), its response time and the consumables (e.g., calibration gases and filters). Additionally, operating temperatures and cooling requirements (e.g., liquid nitrogen) can limit both, the feasibility of field measurements and the analysers stability.
- **Cylinder treatment**
Careful cylinder treatment is recommended, e.g., following the recommendations by Socki et al., (2020). We further recommend reducing moisture levels below $3 \mu\text{mol/mol}$.

i) CO₂ in air mixtures

For CO₂ in air mixtures, we recommend pressures above 10 bar, as composition changes were observed at lower pressures.

ii) Pure CO₂ cylinders

As discussed in detail by Socki and Jacksier, (2021),

- Pressures should be chosen far below the saturation pressure to avoid the formation of a liquid phase (e.g., $p < 34.85$ bar at 0°C), this is particularly relevant for field measurements, if cylinders are stored at potentially low temperatures (outside), yielding lower saturation pressures (see Table 1).
- cylinders should be stored inside the temperature-controlled monitoring station, if possible, to dampen temperature effects
- cylinders should stabilize at the field site for at least 1-2 days (if stored in cold/hot conditions).

Pressure regulators Using two-stage pressure reducers with low dead volume is recommended, adsorption/desorption effects should be tested for new regulator types.

- **Sampling line**

Analysing fluctuations of p , T and Φ directly at the field site is recommended and a comparison between these fluctuations between lab and field conditions can provide insights into field-specific uncertainty contributions.

Temperature (C)	Saturation pressure (bar)
-25	16.83
-20	19.70
-15	22.91
-10	26.49
-5	30.46
0	34.85
5	39.70
10	45.02
15	50.87

Table 1: CO₂ saturation pressures at different temperatures – data from <https://webbook.nist.gov/chemistry/fluid/>

- **Avoiding memory effects**

To avoid memory effects, the following recommendations, have been proposed (see Braden-Behrens et al 2023)

- evaluate the instrument's response to a step change and choose appropriate flushing times.
- The magnitude of the step change in this evaluation should cover the largest step change occurring in the experiment.
- repeat this evaluation regularly, in particular for static systems, as changes in the pumps effectiveness can influence memory effects.
- evaluate the response of the whole setup including tubing and filters.

5. Exemplary field measurements with OIRS

5.1 Comparing temperature stability under field and lab conditions

As temperature is an important driver of instrument instability, an analysis of the instrument's cell and cavity temperature as well as the ambient temperature at the field site might help to gain insight on the instrument stability (Braden-Behrens et al 2023). Together with partners from Johann Heinrich von Thünen Institute (Braunschweig, Germany), PTB put a Picarro G2201i analyser into a fully insulated temperature-controlled housing. We sampled ambient air in this box under field conditions and compared the resulting dataset to comparable measurements of ambient air under lab conditions performed at PTB. We found that, even if the amplitude of cavity temperature fluctuations was one order of magnitude larger for field conditions, the variability of cavity temperature under field conditions is below 3mK. We did not see any effect of this temperature variability on the observed variability of measured ^{13}C values. T was not significantly larger (see Fig. 1).

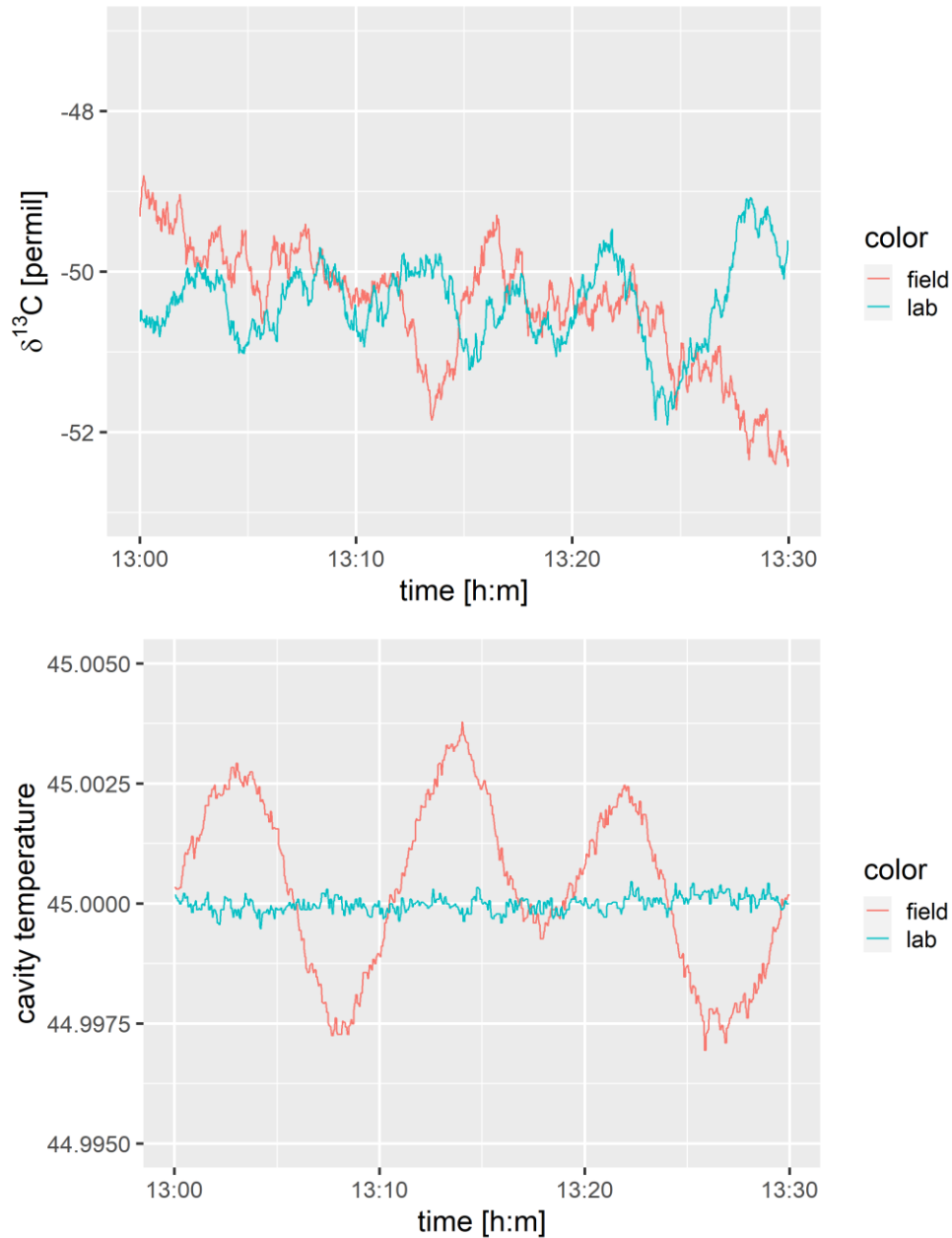


Fig. 1: The top panel shows cavity temperature, and the bottom panel shows the raw delta13C value of the Picarro G2201-i analyzer used in field conditions (red line) and lab conditions (cyan line). While the cavity temperature showed a larger variability under field conditions, the variability of the measured δ values was comparable.

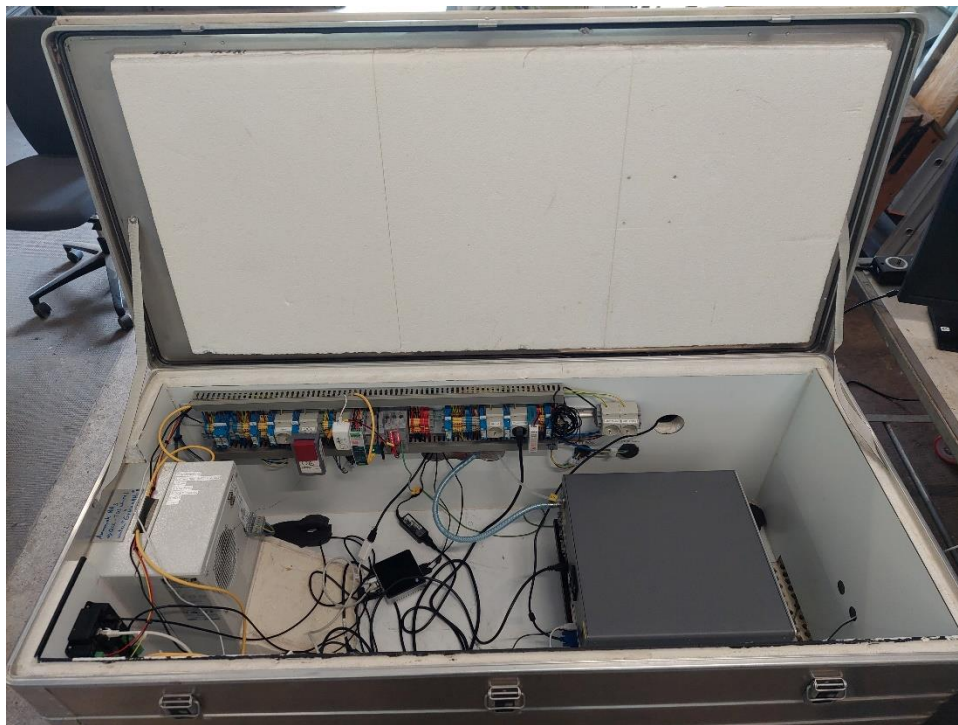


Fig. 2: Fully insulated temperature-controlled housing used by Johann Heinrich von Thünen Institute (Braunschweig, Germany) together with PTB to analyze temperature stability under field conditions.

5.2 Source measurements from the atmosphere (UEF)

UEF placed a Picarro G2201-i at a remote peatland site (ICOS Lompolojännkä) to measure the source $\delta^{13}\text{C}(\text{CH}_4)$ value and its variation through the progression of the growth season. The site had a permanent climate-controlled measurement cabin and reliable power supply, but we had no remote access to the instrument. The instrument was connected to an ambient air inlet at 1m height. No reference gases at atmospheric concentration were available at the time of the campaign. Instead, we used a cylinder of compressed (technical) air as a secondary standard for drift control that was analysed twice per day for one hour.

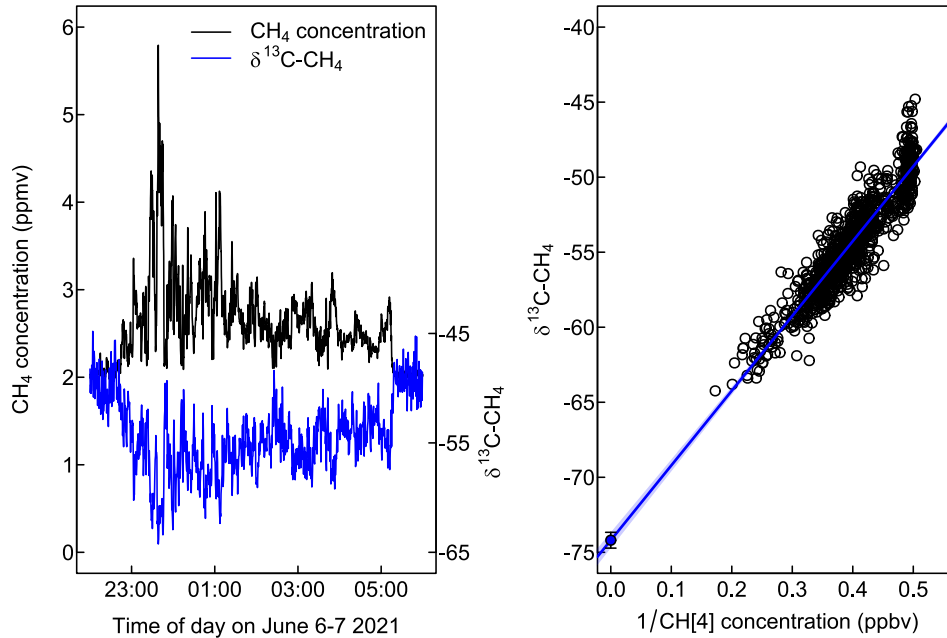


Fig. 3: Example of methane concentrations and $\delta^{13}\text{C-CH}_4$ (left) and Keeling plot (right) observed during over 8 hours measurement when a nighttime boundary layer led to local CH_4 accumulation. $\delta^{13}\text{C-CH}_4$ values represent 30-second averages. The open blue circle with error bars indicates the estimated intercept, i.e., the estimates source $\delta^{13}\text{C-CH}_4$ value. Error bars and the shaded are indicate two standard error uncertainty.

5.3 Ambient CO₂ measurements from atmosphere (VTT)

VTT developed a field-deployable tunable laser direct absorption spectrometer (TDLAS) based on a multi-pass cell (MPC), and a mid-infrared quantum cascade laser (QCL). For field measurements, the device was moved to the ICOS station in Helsinki (SMEAR – III station). The experiments were carried out in collaboration with University of Helsinki and ICOS. Continuous and uninterrupted measurements were carried out at the station for approximately 12 days.

For a referenced measurement three consecutive measurements (reference / sample / reference) are required, to mitigate the effect of drifts affecting the signal for integration times longer than 20 seconds (as shown in Task A3.1.6). Between the measurements there is a 10 second dead time for switching between the gases. This implies that the precision of a single calibration measurement is worse than the precision at the optimum integration time of 10 seconds. Multiple consecutive referenced measurements can be made at a rate of 80 seconds.

To assess the precision of the spectrometer for referenced measurements, we used instrument air as a reference gas and used the lab air as sample. The sample-reference

measurements were made after an interval of 40 seconds and each reference measurement was used twice for calibration. The fit results of the data and the corresponding concentration of the whole data set is shown in Figure 4. The Allan plot for the whole data set is also plotted in Figure 5.

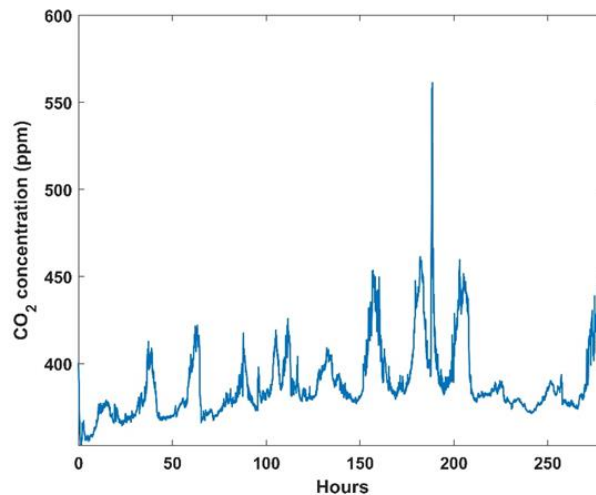


Fig. 4: The CO₂ sample concentration for ~ 12 days of measurements is plotted.

From Figure 4, we can say that there are many spikes in the concentration measurements. It is, however, difficult to identify if the spikes arise due to actual isotopologue fluctuations or instrument uncertainty and errors. We checked the stable region measurement, and it shows better Allan deviation. This is plotted in Figure 6. The standard deviation of the measurements at an averaging time of 80 seconds is 0.6 ‰ and 0.4 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ which goes down to 0.2 ‰ and 0.2 ‰ at an averaging time of 560 seconds.

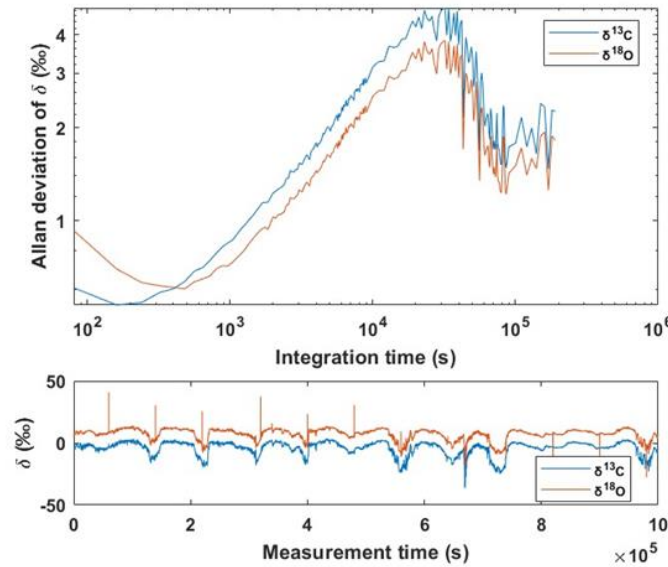


Fig. 5: The Allan deviation of the whole data set is shown in the upper panel and δ (‰) for ^{13}C and ^{18}O plotted in blue and red respectively is shown in the lower panel.

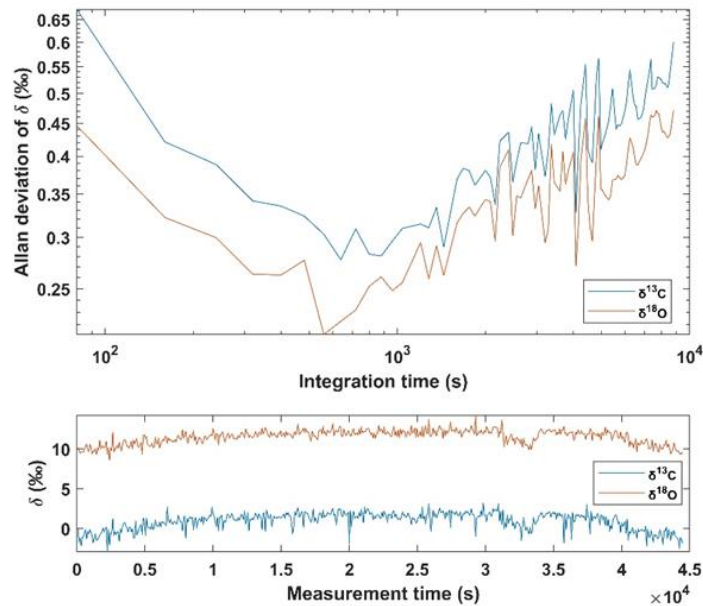


Fig. 6: The Allan deviation of δ values of ^{13}C and ^{18}O are plotted in the upper panel of Figure 3. This plot is for the stable concentration region i.e., 20 – 32.5 hours of measurements time from the whole data set. The δ values of ^{13}C and ^{18}O are plotted in blue and red respectively in the lower panel.

6. Options to quantify OIRS-IRMS in field compatibility

Several research groups have conducted comparison measurements between OIRS (preconcentration-OIRS, CRDS) and IRMS for isotopic composition and / or OIRS and alternative methods for CO₂ and CH₄ concentrations. Independent measurements in the field and in the lab (sampling flasks) have also been compared. One of this example research is from Chiara Uglietti et al 2008 where, they make real-time measurements of atmospheric CO₂ and O₂ at Jungfraujoch station, Switzerland and compare it to the corresponding flask measurements. There was a good agreement in CO₂ measurements while, the O₂ measurements matched moderately. Another example of comparison flask measurements is shown in an article by I. T. van der Laan-Luijkx et al., 2013). Here, a summary of measurements run over 4 years at three European universities (the University of Bern, Switzerland, the University of Groningen, the Netherlands and the Max Planck Institute for Biogeochemistry in Jena, Germany) is presented. An intercomparison of CO₂, $\delta(O_2/N_2)$ and $\delta^{13}CO_2$ depicts that there is a requirement of regular intercomparisons between different laboratory measurements. Another comparison of flask and in-situ measurements at a city in northeastern Poland have been presented by H.Chen et al., 2012.

We aimed at performing similar comparison flask and IRMS measurements during the STELLAR project but could not do so due to time constraint. However, it could be very interesting to perform such studies in the future projects. We, looked into the following measurements and comparisons:

6.1 Example 1: Compatability of analytical techniques for CH₄ isotope measurements

Eyer et al. (2016) assessed the compatibility of different analytical techniques for CH₄ isotope measurements on the ambient air as shown in Fig. 7. Measurements were done either on identical gas samples, i.e., for IRMS measurements of glass flask samples by UU (Institute for Marine and Atmospheric research Utrecht (IMAU) of Utrecht University) and MPI (table Isotope Laboratory of Max Planck Institute (MPI) for Biogeochemistry), or on simultaneously collected ambient air samples, i.e., for all other techniques (laser spectrometers and bag samples/IRMS). Isotope data of all techniques were offset-corrected to account for systematic differences (scale differences and instrumental artifacts) between individual laboratory results.

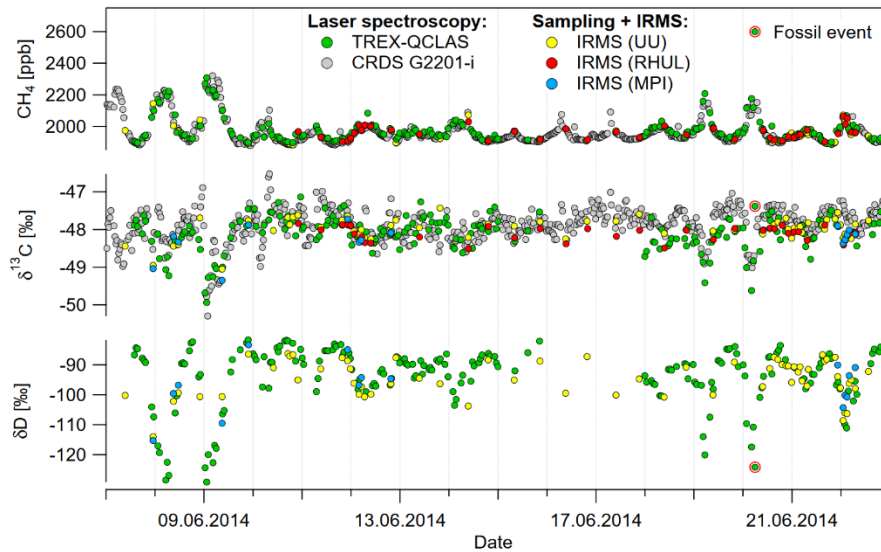


Fig. 7: CH_4 mole fractions and isotopic composition analyzed during the interlaboratory comparison campaign in real time by the laser spectroscopic techniques: TREX-QCLAS (Empa) (CH_4 , $\delta^{13}\text{C}$, δD), CRDS G2201-i (CH_4 , $\delta^{13}\text{C}$), and on glass flask/bag samples with IRMS by UU (CH_4 , $\delta^{13}\text{C}$, δD), MPI (CH_4 , $\delta^{13}\text{C}$, δD) and RHUL (Greenhouse Gas Laboratory, Department of Earth Sciences (GGLES) of the Royal Holloway University of London) (CH_4 , $\delta^{13}\text{C}$). (Reproduced from Eyer et al. (2016)).

Data display a generally good compatibility of techniques. The standard deviation of differences in $\delta^{13}\text{C}\text{-CH}_4$ is lowest for the two IRMS techniques that also measured identical samples, intermediate for TREX-QCLAS vs. IRMS and highest for CRDS vs. IRMS, the same order as observed for the repeatability of techniques. For $\delta\text{D}\text{-CH}_4$ the standard deviation of differences between TREX-QCLAS and the UU IRMS is comparable or smaller than the one corresponding to the two IRMS systems (UU and MPI), which is also in agreement with repeatability results.

6.2 Example 2: OIRS IRMS comparison measurements of isotope ratios

i) Measurements at NPL

Preconcentration-OIRS has been compared with IRMS under field conditions using ambient amount fraction mixtures prepared from pure methane in a synthetic air matrix. Two mixtures were prepared in September 2022, and January 2023 that were measured sequentially to also identify any fractionation effects during storage. The measurement timeseries is shown in Figure 8. These measurements are calibrated using the PRMs developed in this project but have not been offset-corrected for instrumental artefacts and show some fractionation in $\delta^{13}\text{C}(\text{CH}_4)$ due to the preconcentrator. For atmospheric

measurements, an ambient working standard is sampled regularly to apply an offset correction using the principle of identical treatment for the atmospheric sample and standard.

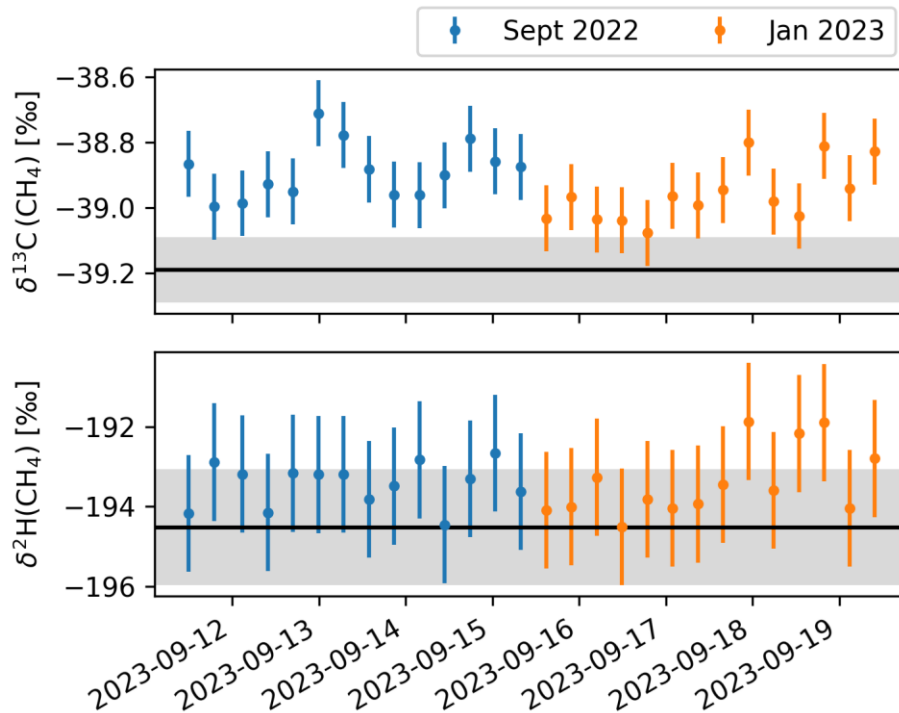


Fig. 8: Repeated measurements of a cylinder of ambient amount fraction using the Boreas preconcentrator-OIRS. The two colors indicate mixtures produced from the same high-purity CH_4 source 4 months apart. The solid lines indicate the isotope ratios assigned by IRMS and the shading is the uncertainty. The error bars on the measurements indicate the OIRS calibration uncertainty, propagated from the uncertainty in the PRMs.

The summary of the repeated trials is given in Table 2. There is a difference between the means of $\delta^{13}\text{C}(\text{CH}_4)$ ($t(25.9) = 2.18$, $p = 0.04$), but no significant difference between $\delta^2\text{H}(\text{CH}_4)$ ($t(21.7) = 0.17$, $p = 0.87$).

Tank prepared	$\delta^{13}\text{C}(\text{CH}_4)$	s.d.	$\delta^2\text{H}(\text{CH}_4)$	s.d.	N
Sept 2022	-38.89‰	0.08‰	-193.44‰	0.54‰	14
Jan 2023	-38.95‰	0.09‰	-193.39‰	0.87‰	14

Table 2: Summary of the repeated trial measurements.

ii) Measurements at BCG-IsoLab

The $\delta^{13}\text{C}$ - and $\delta^2\text{H-CH}_4$ stable isotope composition of two pure methane sources was measured at the BCG-IsoLab. The $\delta^{13}\text{C-CH}_4$ isotopic composition was analysed on a Delta+XL isotope ratio mass spectrometer coupled to an elemental analyser, and the $\delta^2\text{H-CH}_4$ isotope ratio was analysed on a DeltaV Advantage coupled to a high temperature pyrolysis oven. The method has been described in Sperlich et al. (2016, 2020). $\delta^{13}\text{C-CH}_4$ measurements are standardised using IAEA-603 ($+2.46 \pm 0.01\text{‰}$) and NBS22 ($-30.03 \pm 0.05\text{‰}$) and reported on the VPDB-LSVEC scale (Brand et al., 2014). There is a current discussion on whether the VPDB-LSVEC scale should be discontinued, and a new scale implemented (Qi et al., 2021; Helie et al., 2021), and so $\delta^{13}\text{C-CH}_4$ are also reported on the VPDB scale using IAEA-603 and USGS44 ($-42.08 \pm 0.01 \text{‰}$; Qi et al., 2021). The $\delta^2\text{H-CH}_4$ values were analysed against VSMOW2 ($0 \pm 0.3 \text{‰}$) and SLAP2 ($-427.5 \text{‰} \pm 0.3$) water standards and are reported on the VSMOW/SLAP scale.

Methane at concentrations between 1.8 and 2.2 ppm in air, or air like matrix was analysed using “iSAAC” (The integrated System for Analysis of Atmospheric Constituents). The system is designed to separate methane from the air matrix and trap it. Subsequently the methane is either oxidised to CO_2 , or reduced to H_2 , to measure the isotopes or methane. The method has been described in Brand et al., 2016.

6.3 Example 3: Comparison measurements of amount fraction

OIRS instruments can measure the total amount fraction of methane, in addition to the isotope ratio. In-field verification of these measurements, against a reference instrument, provide a test of the instrument performance over a wide range of conditions from baseline to polluted air masses. This comparison has been performed for the NPL preconcentrator OIRS against a Picarro G2401 (see Picarro 2021) at the Heathfield atmospheric monitoring station. Both preconcentrator-OIRS and reference G5310 (see Picarro 2023) sample air from the same inlet at 100 m above ground level, which is continuously pumped by a diaphragm pump at 20 L min^{-1} . This is much faster than the sample rate of either instrument, so both can operate independently on effectively the same air sample. The G2401 is calibrated using a reference tank filled with background ambient air that has been value assigned for CH_4 to the WMO- CH_4 -X2004A scale. This instrument measures continuously, and the results are aggregated into one-minute averages. The preconcentrator-OIRS collects an air sample for 10 minutes during the 70-minute duration trapping cycle. This difference in sample timing means that each instrument could sample a different air mass, where the CH_4 amount fraction can change rapidly during a pollution event. The data are matched for sampling time so that only the G2401 measurements made while the trap is open are kept, then each of these subsets are averaged.

The results for one year of measurements between June 2022 and June 2023 are plotted in Figure 9 as scatter points, with error bars representing the calibration uncertainty of the OIRS measurement. This shows that the two techniques are equivalent (correlation coefficient $r = 0.937$), and there are no artifacts from preconcentration such as breakthrough and loss of sample at the highest amount fraction.

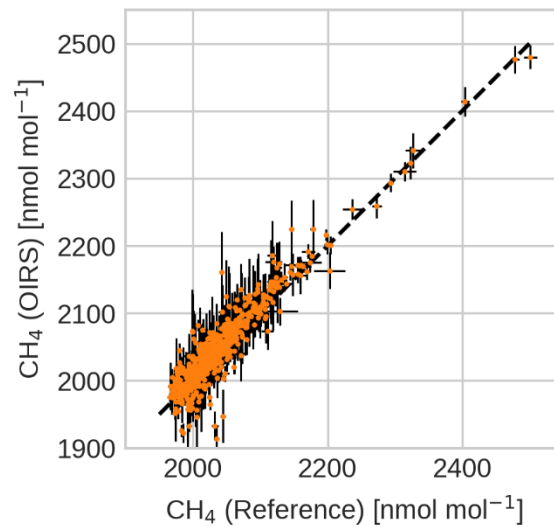


Fig. 9: Scatter plot of measurement of the amount fraction of CH₄ in an ambient air sample simultaneously by a Picarro G2401 (reference instrument, x axis), and the Boreas preconcentrator-OIRS (y axis) between June 2022 and June 2023. The dotted line represents equivalence of the two measurements.

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References:

1. J. Braden-Behrens, A. Emad, V. Ebert, F. Durbiano, G. Li, H. Moosen, J. Nwaboh, S. Pavarelli, F. Rolle, M. Sega, P. M. Steur, 'Good practice guide for specification and application of OIRS for atmospheric measurements, including sample handling protocol, optimised analytical procedures, traceability to the international standards and target uncertainties (0.05 ‰ for $\delta^{13}\text{C-CO}_2$ and $\delta^{18}\text{O-CO}_2$)', 2023.
2. Chris Rennick, Tim Arnold, Cam Yeo, Joachim Mohn, Kerstin Zeyer, Jelka Braden-Behrens, Volker Ebert, Anas Emad, Gang Li, Javis Nwaboh, Olav Werhahn, Stefan Persijn, Mehr Fatima, Thomas Hausmaninger, Heike Geilmann, Heiko Moossen, 'Good practice guide for accurate methane isotope ratio measurements using laser spectroscopy: analyser characterisation and statement of uncertainty with a target precision of 0.2 ‰ for $\delta^{13}\text{C}(\text{CH}_4)$ and 1 ‰ for $\delta^2\text{H}(\text{CH}_4)$.' , 2023.
3. https://meta.icos-cp.eu/objects/JUOeklwSb3fh8hdK9eL3_V9V
4. 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Measurement Techniques (GGMT-2019)
5. Eyer, S. and Tuzson, B. and Popa, M. E. and van der Veen, C. and Röckmann, T. and Rothe, M. and Brand, W. A. and Fisher, R. and Lowry, D. and Nisbet, E. G. and Brennwald, M. S. and Harris, E. and Zellweger, C. and Emmenegger, L. and Fischer, H. and Mohn, J. (2016), Real-time analysis of $\delta^{13}\text{C}$ and $\delta\text{D-CH}_4$ in ambient air with laser spectroscopy: method development and first intercomparison results. Atmospheric Measurement Techniques, 9(1), 263-280.
6. Thermo Fisher Scientific. (2016), Delta Ray Series Isotope ratio infrared spectrometer: User Guide. Thermo Scientific.
7. Braden-Behrens, J., Yan, Y., & Knohl, A. (2017), A new instrument for stable isotope measurements of ^{13}C and ^{18}O in CO_2 - instrument performance and ecological application of the Delta Ray IRIS analyzer, Atmospheric Measurement Techniques, 10(11), 4537–4560.
8. PICARRO Inc. (2016). G2201-i Analyzer Datasheet.
9. Socki, R., Matthew, M., McHale, J., Sonobe, J., Isaji, M. and Jacksier, T. (2020), Enhanced Stability of Stable Isotopic Gases, ACS Omega, 5(29), 17926–17930, doi:10.1021/acsomega.0c00839, 2020.
10. Socki, Richard A. Socki and Tracey Jacksier (2021). Isotope Fractionation of Gaseous, Supercritical , and Dual-Phase Carbon Dioxide in Pressurized Cylinders Exposed to

- Variable Temperatures, ACS Omega Article ASAP, doi: 10.1021/acsomega.1c00474
Braden-Behrens et. al, 2023, 'Good Practice Guide for CO₂ measurements' MSU EMPIR
11. <https://webbook.nist.gov/chemistry/fluid/>
 12. <https://creativecommons.org/licenses/by/3.0/>
 13. van der Laan-Luijkx, I. T., van der Laan, S., Uglietti, C., Schibig, M. F., Neubert, R. E. M., Meijer, H. A. J., Brand, W. A., Jordan, A., Richter, J. M., Rothe, M., and Leuenberger (2013), Atmospheric CO₂, δ(O₂/N₂) and δ¹³CO₂ measurements at Jungfrauoch, Switzerland: results from a flask sampling intercomparison program, *Atmospheric Measurement Techniques*, 6(7), 1805–1815.
 14. Chiara Uglietti and Markus Leuenberger and Francesco L. Valentino (2008), Comparison between real time and flask measurements of atmospheric O₂ and CO₂ performed at the High Altitude Research Station Jungfrauoch, Switzerland, *Science of The Total Environment*, 391(2), 196-202.
 15. Chen, H., Winderlich, J., Gerbig, C., Katrynski, K., Jordan, A., and Heimann, M (2012), Validation of routine continuous airborne CO₂ observations near the Bialystok Tall Tower, *Atmospheric Measurement Techniques*, 5(4), 873–889.
 16. Sperlich, P. and Uitslag, N. A. M. and Richter, J. M. and Rothe, M. and Geilmann, H. and van der Veen, C. and Röckmann, T. and Blunier, T. and Brand, W. A. (2016). Development and evaluation of a suite of isotope reference gases for methane in air. *Atmospheric Measurement Techniques*, 9(1), 3717-3737.
 17. Sperlich, P., Moossen, H., Geilmann, H., Bury, S.J., Brown, J.C.S., Moss, R.C., Brailsford, G.W. and Brand, W.A. (2021), A robust method for direct calibration of isotope ratios in gases against liquid/solid reference materials, including a laboratory comparison for δ¹³C-CH₄. *Rapid Commun Mass Spectrom*, 35:e8944. <https://doi.org/10.1002/rcm.8944>.
 18. Brand, Willi A., Coplen, Tyler B., Vogl, Jochen, Rosner, Martin and Prohaska (2014), Thomas, Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report), *Pure and Applied Chemistry*, 86(3), 425-467. <https://doi.org/10.1515/pac-2013-1023>.
 19. Qi, H, Moossen, H, Meijer, HAJ, et al. USGS44 (2021), A new high-purity calcium carbonate reference material for δ¹³C measurements. *Rapid Commun Mass Spectrom.*; 35:e9006. <https://doi.org/10.1002/rcm.9006>.
 20. Jean-François Hélie, Agnieszka Adamowicz-Walczak, Paul Middlestead, Michelle M.G. Chartrand, Zoltán Mester, and Juris Meija (2021), Discontinuity in the Realization of the Vienna Pee Dee Belemnite Carbon Isotope Ratio Scale, *Analytical Chemistry* 93(31), 10740-10743.
 21. Brand WA, Rothe M, Sperlich P, Strube M, Wendeborg M. (2016), Automated simultaneous measurement of the δ(13) C and δ(2) H values of methane and the δ(13) C and δ(18) O values of carbon dioxide in flask air samples using a new multi cryo-trap/gas chromatography/isotope ratio mass spectrometry system, *Rapid Commun Mass Spectrom*. 30(13),1523-39, doi: 10.1002/rcm.7587. PMID: 27321840.
 22. PICARRO Inc. (2021). G2401 Analyzer Datasheet.
 23. PICARRO Inc. (2023). G5310 Analyzer Datasheet.