



Data
Models
Inventories

PARIS

Process Attribution of Regional Emissions

GA 101081430, RIA

New Boreas instrument constructed

Milestone 13

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Horizon Europe Cluster 5: Climate, energy and mobility

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1. Changes with respect to the DoA (Description of the Action)

N/A

2. Dissemination and uptake

The results of this milestone will be of direct use to partners within PARIS involved in WP4 tasks, which rely on high-frequency CH_4 , C_2H_6 and $\delta^{13}\text{C}(\text{CH}_4)$ observations for model–data comparisons and regional inversions. The construction and development of this instrument will lead to deployment at a UK atmospheric research station that will enable improved constraints on fossil-fuel methane emissions in subsequent project tasks.

3. Short Summary of results

Close collaboration between the University of Bristol and National Physical Laboratory (NPL) has resulted in the characterization of an Aerodyne TILDAS-FD-142 for the purpose of the measurement of methane isotopologues ($^{12}\text{CH}_4$, $^{13}\text{CH}_4$), ethane (C_2H_6) and calculated methane isotope ratio ($\delta^{13}\text{C}$). A calibration and sampling scheme has been developed, using calibration standards developed by NPL and the University of East Anglia (UEA). Short and long-term precisions have been characterized in the laboratory at the University of Bristol. Long-term precisions for CH_4 and C_2H_6 are determined on average to be 11.06 ppt and 0.19 ppb respectively, values of which are directly comparable to or better than studies carried out with similar absorption spectrometers (Kostinek et al., 2019; Commane et al., 2023). For $\delta^{13}\text{C}(\text{CH}_4)$, we report a precision of 0.61 ‰ which is useful for resolving atmospheric variability in the measurements larger than 10 ‰. Collaboration with the instrument manufacturer is in progress to ascertain an improvement to this precision. While the precisions on the mixing ratio of individual CH_4 isotopologues are sufficient, this issue is attributed to pressure and/or temperature spectroscopic broadening effects on the $^{13}\text{CH}_4$ absorption line, propagating through the isotope ratio where the effects become more apparent. This issue is currently being addressed with the help of the instrument manufacturer. The instrument has been deployed to the SOAR site where another performance analysis has been carried out to determine the effect of laboratory temperature control on the resolved measurements and, in general, identify and correct for any systematic differences in operation.

4. Evidence of accomplishment

4.1 Introduction | Background of the milestone

The composition of stable carbon isotopes in emitted atmospheric methane (CH_4) is determined by different microbial, pyrogenic and fossil fuel production mechanisms. These processes cause both carbon and hydrogen in CH_4 to undergo various isotopic fractionation effects which are quantifiable by the relative abundance of heavy $^{13}\text{CH}_4$ to light $^{12}\text{CH}_4$ isotopes in a sample compared to a standard. This makes resolved isotope ratios a useful tool in the disaggregation of anthropogenic CH_4 emissions. Overlaps in these source signatures between categories can introduce difficulty when attributing sources to a measured plume. Trace gases are used to aid source apportionment as they provide an extra dimension of constraint. Ethane (C_2H_6) is one such gas, emitted predominantly by gas distribution in distinct ratios to CH_4 and thus is used as a vector to constrain fossil fuel methane. Recent work by Ramsden (2022) demonstrates that incorporating atmospheric C_2H_6 measurements into methane inversions substantially improves the ability to quantify UK fossil-fuel CH_4 emissions. Results from these simulated tests in the UK region suggest ethane reduces posterior fossil-fuel CH_4 uncertainties by ~15% on average and up to 35% compared with CH_4 -only inversions. Expanding the spatial coverage of C_2H_6 observations would further improve constraints by providing additional information on regional variations in the ethane:methane emission ratio and refining spatial separation between fossil-fuel and biological CH_4 sources.

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Therefore, more spatially distributed C_2H_6 measurements enhance the inversion's ability to characterise spatial heterogeneity, reduce dependence on prior assumptions, and improve propagation of uncertainty in the emission ratio hyperparameter.

Towards this goal, we have procured an Aerodyne TILDAS laser absorption spectrometer, capable of measuring methane isotopologues ($^{12}CH_4$ and $^{13}CH_4$), C_2H_6 and resolved carbon-13 isotope ratio ($\delta^{13}C(CH_4)$). In this report, we present a brief review of results from extensive laboratory testing of this new laser absorption spectrometer. The purpose of this testing was to characterise the instrument and develop a sampling methodology to apply ready for deployment to the SOAR tall-tower site. Moreover, we present the methodology used to perform calibration, develop a sampling scheme and understand instrument performance.

4.2 Scope of the milestone

This milestone is intended to detail the development and characterisation of the new Aerodyne TILDAS-FD-142 laser absorption spectrometer and the preparations carried out before deployment took place.

4.3 Content of the milestone

Significant work was undertaken in the lab to characterize the Aerodyne TILDAS and develop a sampling methodology, ready for deployment to Invergowie.

The instrument is operated by a combination of TDLWintel software for spectral acquisition and GCWerks for automated run sequencing. Resulting measurement data is synced to a remote server operated by the University of Bristol ACRG group where a series of Python scripts periodically calibrate and drift-correct the data.

The short-term stability and precisions for each species measured were evaluated in the lab using Allan-Deviation as a statistical measure, allowing the characterization of noise behaviours over different averaging times (τ).

A calibration gas with known ambient amount fractions for each species is expanded into the cell and held to be measured for ~ 6 hours. The square-root of the mean-squared difference between adjacent time-averaged measurements is calculated on the raw data and plotted on a log-log scale against averaging time to identify dominant noise sources. Fig. 1 shows the Allan-Deviation analysis carried out for $^{12}CH_4$, $^{13}CH_4$ and C_2H_6 respectively. The averaging times applied to the measurements are given in Table 1, alongside the corresponding short-term noise for each species.

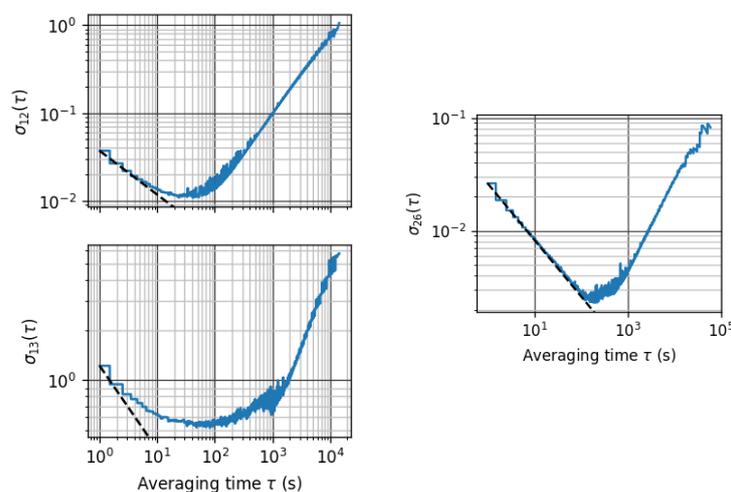


Fig. 1: Allan-Deviation plot for carbon-12 methane (upper left), carbon-13 methane (lower left) and ethane (centre right) in laboratory testing. The minimum of the curve (blue) represents the optimal averaging time and corresponding short-term precision. The dashed black line denotes flicker noise as the dominant noise type.

Table 1: Optimal averaging time per measurement period applied to the methodology. The minimum AD at the corresponding averaging time gives the short-term precision, encompassing all noise sources.

Species	Optimal averaging time τ (s)	Minimum $\sigma(AD)$
$^{12}CH_4$	41	10.8 ppt
$^{13}CH_4$	81	0.52 ppb (~ 5.4 ppt)
C_2H_6	201	2.3 ppt

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The precision analysis shows that each species reaches a well-defined minimum with optimal averaging times ranging from 40s to 201s dependent on species. The absorption line for $^{13}\text{CH}_4$ was chosen to be highly sensitive to the lower abundance in the atmosphere, therefore the raw $^{13}\text{CH}_4$ amount fraction and precision is reported at $\sim 95\times$ the true atmospheric value. After calibration, the equivalent short-term precision is proportionally smaller than the reported raw value at ~ 5.4 ppt. The short-term precisions reported here are comparable to studies published utilizing similar laser absorption instrumentation (Kostinck et al., 2019; Commane et al., 2023).

Each measurement made of a sample within operational conditions uses ~ 372 mL of gas. Calibration by measurement of the 10-20 L standards before each air measurement would therefore reduce the life of the tanks significantly, consequently increasing cost. Additionally, the temporal resolution of the instrument would suffer consequently. Hence, it becomes clear that understanding the optimal calibration frequency is crucial to reach a balance of cost without suffering a significant decrease in precision. To investigate this, the standards detailed in Table 2 were individually analysed in the sampling cell at 309 Torr and measured in consecutive sequence (CS-ML > CS-MH > CS-MM) over ~ 40 hours. The CS-ML and CS-MH standards were used to linearly calibrate the mid-range standard, acting as the air measurement. The slope of the linear fit (purple solid line) is calculated by dividing the difference between the known (certified) concentrations by the difference between the measured values of the tanks. The intercept is calculated by subtracting the product of the calculated slope by the assigned CS-MH value from the measured CS-MH value. Each target species is then assigned a calculated slope and intercept value set such that they can be calibrated individually. Four different methods of calibration were applied to the dataset as follows:

- **Repeated calculation:** The slope and intercept of the linear calibration is re-calculated for each air measurement in the period of analysis.
- **Static intercept:** The intercept value of the linear calibration is kept static as calculated from the first run of calibration standards in the analysis period. The slope is re-calculated for each air measurement.
- **Static slope:** The slope value of the linear calibration is kept static as calculated from the first run of calibration standards in the analysis period. The intercept is re-calculated for each air measurement.
- **First run calibration:** The slope and intercept value from the first run of calibration standards is applied to all air measurements in the analysis period.

Here, the aims were to a) investigate the maximum possible number of air measurements before drift and b) to assess whether the slope and intercept of the instrument's linear calibration can be constrained using a varied set of calibration tanks, enabling less frequent full calibrations and potentially allowing independent adjustment of slope and intercept at staggered intervals. Fig. 2 shows the results of this test. As expected, calibration carried out on the first run onwards is dominated quickly by drift over all species. In all species, the calibration is most stable when only correcting for the intercept bias and carrying forward the slope, with $^{12}\text{CH}_4$ bracketing the number of runs using this method before drift dominates the measurements. This number of runs is equivalent to ~ 24 hours, and therefore we apply a daily calibration to the instrument.

We therefore calibrate each species using a two-point calibration, utilizing calibration standards that span the expected amount fraction range to be measured. These standards are detailed in Table 2. The CH_4 calibration standards (CS-ML, CS-MM, CS-MH) were prepared gravimetrically from an isotopically characterized parent by NPL and therefore have an associated isotope ratio value of -39.07% . Amount fractions of CH_4 here span from 1.8-2.5 ppm in a synthetic air matrix. The three C_2H_6 calibration standards (CS-EL, CS-EM, CS-EH) were prepared by UEA in air processed by a zero-air generator (ZAG). The amount fractions of C_2H_6 here were verified by repeated measurement via Medusa GC-MS with traceability to the AGAGE scale value. For each species respectively, CS-MM and CS-EM are used to track repeatability.

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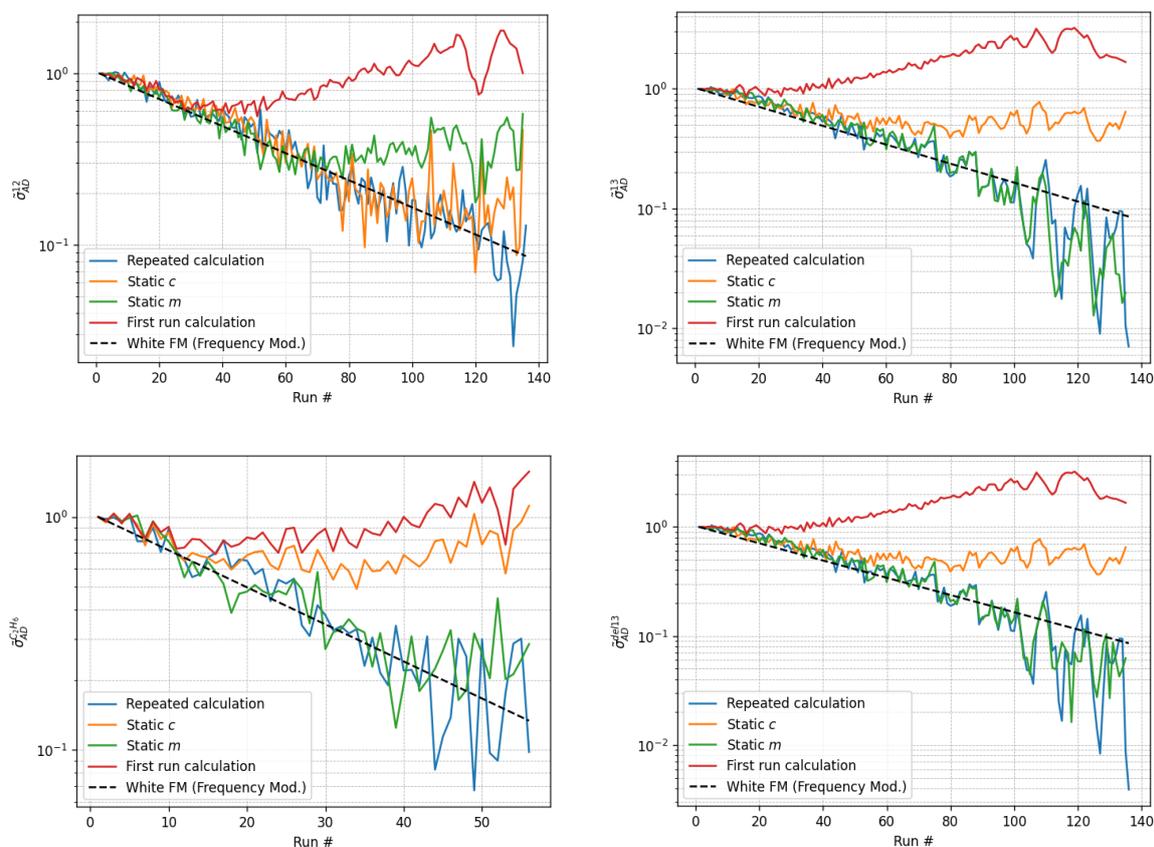


Fig. 2: Log-log Allan deviation plots of (top left) $^{12}\text{CH}_4$, (top right) $^{13}\text{CH}_4$ and (bottom centre) $\delta^{13}\text{C}(\text{CH}_4)$ as a function of the number of measurement cycles in the timeseries for each calibration scenario. The dashed black line denotes white frequency modulation (FM) noise and serves as a diagnostic reference indicating uncorrelated noise.

Table 2: Amount fractions of the calibration gases used for the calibration and characterization of the TILDAS. n/a = not applicable.

Tank name	Type	CH_4 (ppb)	C_2H_6 (ppb)	$\delta^{13}\text{C}(\text{CH}_4)$ (‰)
CS-ML	Methane in synthetic air, low	1815.0	n/a	-39.07
CS-MM	Methane in synthetic air, mid	2008.8	n/a	-39.07
CS-MH	Methane in synthetic air, high	2515.0	n/a	-39.07
CS-EL	Ethane in zero air, low	n/a	1.84	n/a
CS-EM	Ethane in zero air, mid	n/a	2.63	n/a
CS-EH	Ethane in zero air, high	n/a	8.79	n/a
UOB-101	Working standard	2043.0	2.12	-47.96

A tank of dry whole air filled at the University of Bristol, UOB-101, is used to track and correct for instrument drift. The isotope ratio value here was verified by measurement on the Isotope Ratio Mass Spectrometry (IRMS) system at Royal Holloway University London (RHUL). The Medusa GC-MS was used to verify C_2H_6 content in this cylinder, while CH_4 content was verified via Picarro G2401 at the University of Bristol. Based on the results detailed in Fig. 2, we measure the suite calibration standards once daily, while UOB-101 is measured hourly to correct for instrument drift. Each measurement takes 8 minutes from sample preparation to the end of the sample integration within the cell. We take an average over each measurement equal to the optimal averaging time for each species detailed in Table 1, giving us the optimal precision per measurement. Ultimately, the instrument can measure 6-7 air samples per hour.

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The long-term precisions are calculated by evaluating the 4-hour rolling standard deviations of a calibrated tank of whole air. We report the long-term precisions of each species as follows:

- CH₄: 0.19 ppb
- C₂H₆: 11.06 ppt
- δ¹³C(CH₄): 0.61 ‰

Here, amount fraction measurements are sufficient for evaluating measurements from background to large enhancements. Enhancements in the isotope ratio above 10 ‰ are expected to be resolved reliably at this stage which correspond to the attribution of major source categories (microbial, fossil fuel). We expect an improvement in this outcome after review with the instrument manufacturer which is ongoing.

We encountered several operational issues during laboratory testing that were resolved with the aid of the instrument manufacturer. One such issue was electrical noise complications causing housekeeping variable measurements such as pressure and temperature to experience periodic noise, consequently affecting the ability of the instruments spectral acquisition software to correct for these broadening effects. Other issues include unusual spectral effects pertaining to insufficient etalon tuning rate procedures and poor pressure fill repeatability. These issues did not impact the expected deployment date and were resolved in a matter of months. This, alongside the completion of performance, calibration and sample sequence testing, meant the instrument could be deployed in November 2025. A separate milestone report (MS14) details the deployment and preliminary timeseries analyses from the first month of data.

4.4 Conclusion and possible impact

We have demonstrated short- and long-term performance for CH₄ and C₂H₆ and provided an overview of the methodology used to determine these performance metrics. We have developed a detailed calibration scheme, minimising the effects of long-term drift and gas usage. Challenges remain for δ¹³C(CH₄) precision; however, these are understood and currently being addressed in collaboration with the manufacturer. The results of this milestone report directly relate to the deployment of the instrument to the SOAR tall-tower site in Invergowrie, Scotland, which was completed in November 2025.

The new dataset will enable improved inversion constraints on fossil-fuel versus microbial methane sources in the UK, directly supporting the project's goal of advancing process-level attribution of emissions. The expanded spatial coverage of ethane will enhance the robustness of inversion frameworks by supplying an additional tracer for distinguishing fossil-fuel contributions. As a consequence of this laboratory testing procedure, the deployment will contribute valuable evidence to ongoing efforts to harmonize mid-IR spectroscopic techniques across laboratories and supports improved national greenhouse-gas inventories. Overall implications of deployment are detailed in the MS14 report.

4.5 References

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5. History of the document

Version	Author(s)	Date	Changes
1.0	Yeo, Ganesan, Rennick	25 January 2025	First draft