#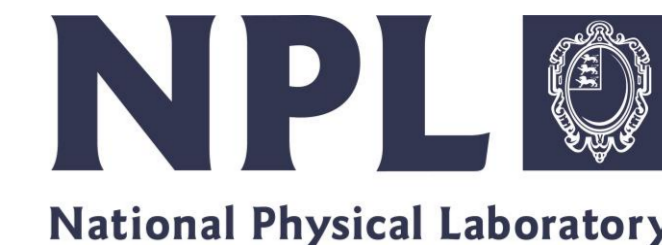 Calibration of Boreas: a new laser-based instrument for in-situ automated measurement of δ $^{13}$C (CH$_4$) and δ $^2$H (CH$_4$) isotope ratios in methane

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**Collaborators**

WMO · FAAM · KRISS · BOC · CEN · ISO · Aerodyne · ABB · NU Instruments · SIAD · LI-COR · NIPPON · Masaryk University · NIWA · Krakow University of Science and Technology · CNR-Institute for Atmospheric Pollution (Italy) · IUPAC-CIAAW

**Partners**

| Sample | δ $^{13}$C(CH$_4$) / ‰ | U / ‰ | Std. Dev. (n=26) / ‰ |
|--------|------------------------|-------|----------------------|
| A | -39.17 | 0.07 | 0.063 |
| B | -51.85 | 0.11 | 0.080 |

| Sample | δ $^2$H(CH$_4$) / ‰ | U / ‰ | Std. Dev. (n=26) / ‰ |
|--------|---------------------|-------|----------------------|
| A | -193.52 | 1.04 | 1.08 |
| B | -189.96 | 1.04 | 1.55 |

## Introduction

A limitation to using optical spectroscopy for isotope ratio measurements of atmospheric methane samples is the low amount fraction (approximately 1.85 µmol mol$^{-1}$ in unpolluted air) leads to low signal levels that limit the measurement uncertainty. The Boreas instrument is designed to improve this by separating and preconcentrating methane from an atmospheric sample to around 550 µmol mol$^{-1}$. However, traceable calibration of the laser spectrometer is hindered by the availability of standard gases at this amount fraction.

We have implemented a scheme that uses gravimetric standards prepared from a pure methane parent to calibrate the spectrometer response.
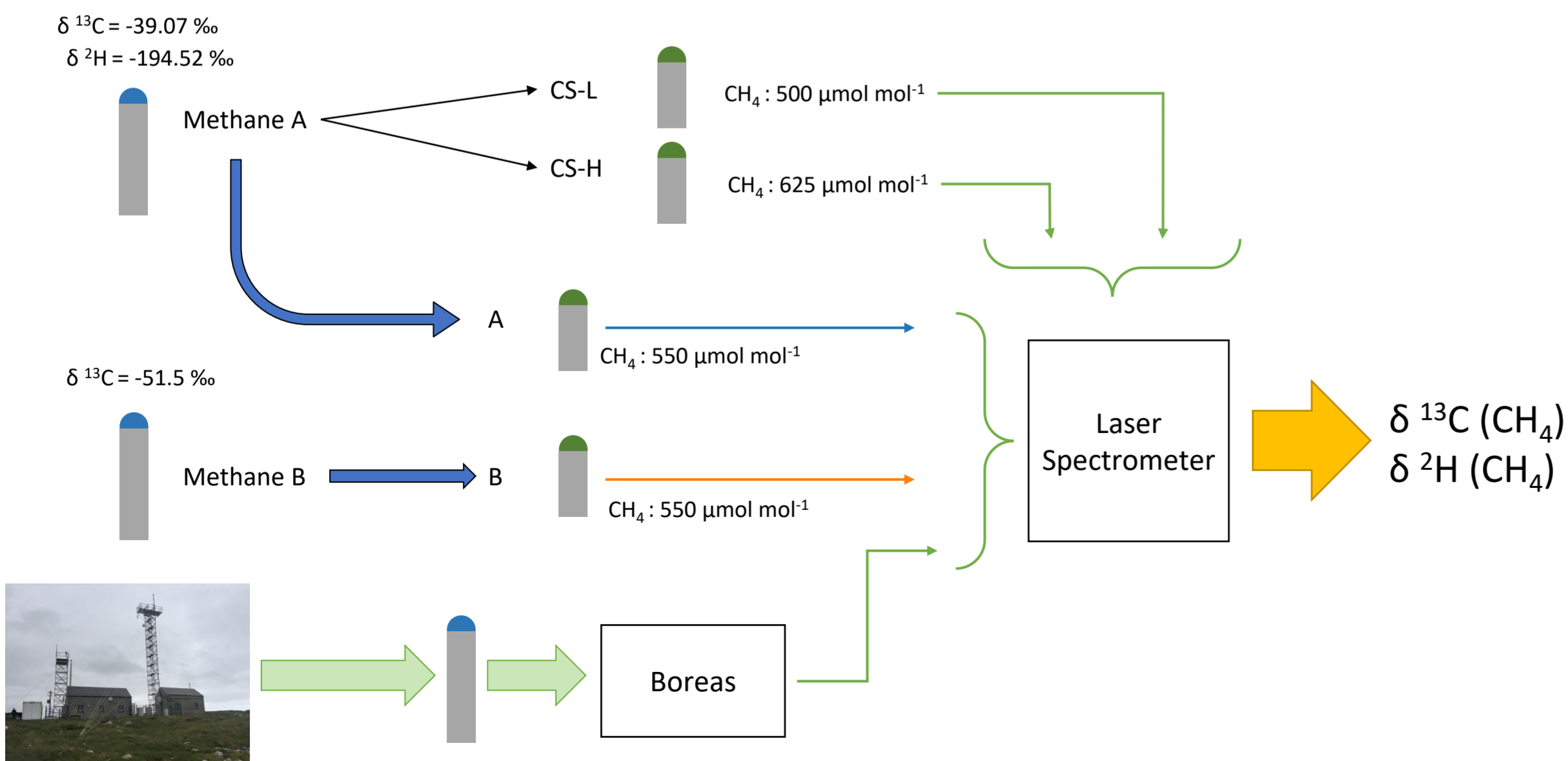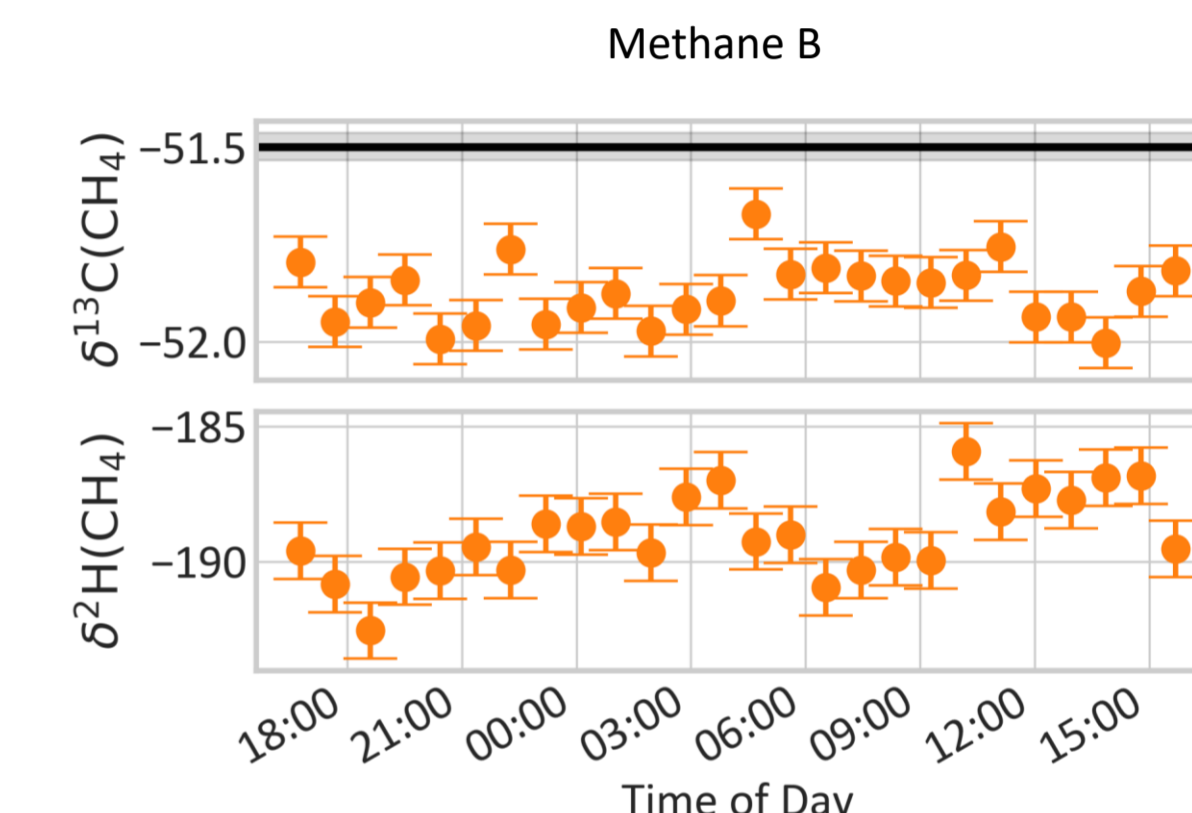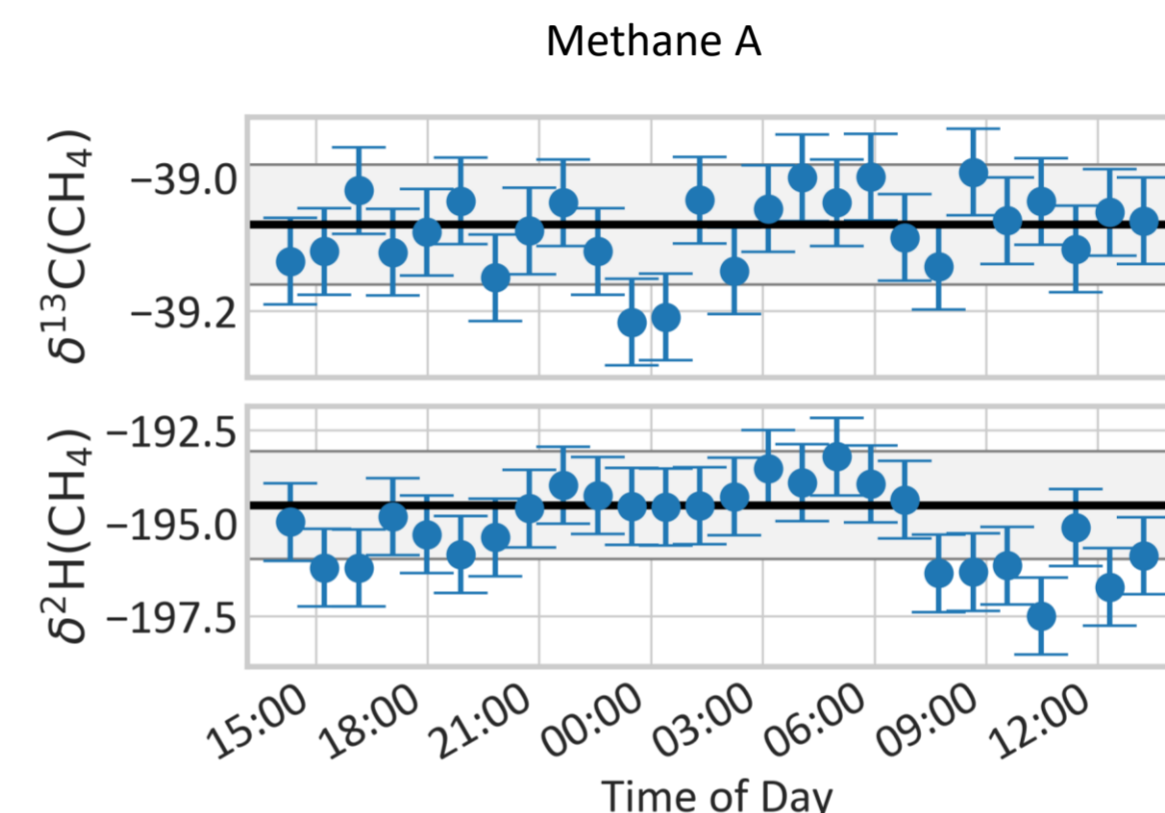
## Calibration

The calibration standards are prepared by dilution of pure methane in nitrogen to make two mixtures that bracket the sample in amount fraction. The standards are analysed by the spectrometer for each air sample, at 1 hour intervals.

The instrument response for each isotopologue is calibrated, then the isotope ratio is calculated from the ratio of isotopologue amount fractions.

The calibrated isotope ratios show good stability with respect to instrumental drift and a value that is comparable with IRMS.

### Methane A



### Methane B



## Discussion

The uncertainty is calculated from the combined uncertainties from preparation of the standards and the instrumental noise.

The dominant contribution to the uncertainty budget is the isotopic signature of the parent methane used to prepare the mixtures. This is assigned by isotope ratio mass spectrometry.

When the isotope ratio of the sample is different to the standard the uncertainty is larger, with the increased contribution coming from the amount fraction of the standards. This is determined from the gravimetric preparation.



δ $^{13}$C = -39.07 ‰
δ $^2$H = -194.52 ‰

Methane A → CS-L
Methane A → CS-H

CH$_4$ : 500 µmol mol$^{-1}$
CH$_4$ : 625 µmol mol$^{-1}$

δ $^{13}$C = -51.5 ‰

A → CH$_4$ : 550 µmol mol$^{-1}$
Methane B → B → CH$_4$ : 550 µmol mol$^{-1}$

Laser Spectrometer → δ $^{13}$C (CH$_4$), δ $^2$H (CH$_4$)

Boreas