Supporting Information

**Boreas: A sample preparation coupled laser spectrometer system for simultaneous high precision in situ analysis of δ^{13}C and δ^{2}H from ambient air methane**

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This file contains the following supporting information: S1 The methane absorption spectrum recorded in this work and details of the fitting procedure; S2 The stability of the spectrometer measurement, used to determine the optimum averaging duration; S3 Mathematical description of the isotopologue and isotope ratio calibration methods; S4 Mass spectrometry measurements and international scale linkage; and S5 Calculation of CH\(_4\) amount fraction in ambient air.
The methane absorption spectrum recorded in this work and details of the fitting procedure.

The light transmission is monitored by a photodiode detector and the output of the photodiode is digitised to produce a spectrum, where the frequency axis is calibrated by an internal reference generated by the regularly spaced fringes transmitted by an etalon. The laser frequencies are swept at a rate of 1.7 kHz and the spectra accumulated every second. Each one-second average spectrum is fitted automatically for the amount fraction of each isotopologue and saved for post-processing. The width of each peak in the high-resolution spectrum depends on sample pressure, temperature, and matrix, and is parameterised with gas-dependent broadening constants. At the amount fraction of standards and samples used here, CH$_4$ self-broadening is negligible, and the peak shape depends on the composition of the matrix gases. The spectrum is fitted using a Voigt profile for each of the absorption lines and a polynomial function for the baseline. The width of each line is the convolution of Doppler and pressure broadening effects, using the measured spectrometer cell temperature and pressure, and the pressure broadening coefficient for each species in air taken from the Hitran database. The position of the entire absorption band is then matched to the recorded spectrum using a strong $^{12}$CH$_4$ line as a reference. The relative position and absorption strength of each line is also taken from the Hitran2016 database, then the profile generated by assuming Beer-Lambert absorption and fitting for the baseline and amount fraction of each species. The advantage of this method is that all absorption lines for a single species are fitted simultaneously, so that interference from overlapping single transitions is much weaker, reducing correlation between recovered amount fractions.

**Figure S1** Spectra recorded by laser 1 (left) and laser 2 (right). Overlaid are simulated spectra for the individual isotopologue, offset vertically for clarity. The dotted line shows where the N$_2$O absorption feature appears, when present. Spectra are simulated for the typical conditions of temperature and pressure in this work and using the Hitran HAPI interface.
S2 The stability of the spectrometer measurement, used to determine the optimum averaging duration

The measured amount fraction is taken as the mean of the instrument response over some averaging period. Increasing the duration of the averaging period will increase the precision up to a point when the measurement is most affected by random noise, after which the precision begins to deteriorate under the influence of drift. This effect is characterised by the Allan-Werle deviation\(^2\) and shown for the three species measured in the calibration target mixture (nominally 550 ppm) in Figure S2. The sample is loaded into the spectrometer cell at a pressure of 28 mbar, then the cell is closed for the 30 hours of measurement.

This shows that random noise dominates the measurement over an interval of about 100 s, giving a limiting measurement precision of 10 ppb for \(^{12}\text{CH}_4\) and \(^{13}\text{CH}_4\); the \(^{12}\text{CH}_3\text{D}\) signal is the smallest of the three and has more noise that dominates the drift for a longer interval, but reaching a lower overall precision of 60 ppb. The drift downwards in reported amount fraction is due to the slow leakage of room air into the cell, diluting the sample.

![Graphs showing amount fraction and Allan-Werle deviation](image)

**Figure S2** Top – the amount fraction reported as a function of time by the spectrometer for the three isotopologues. The plots are shifted to the mean response and have the same vertical scale with the gridlines spaced 10 ppm apart. Bottom - The Allan-Werle deviation for the three measured species is shown as a function of integration time in the lower panels. The dotted line has a gradient of \(1/\sqrt{\mathcal{R}}\) and represents the lower limit arising from random noise, the measurement leaves this line when drift starts to dominate.
S3 Mathematical description of the isotopologue and isotope ratio calibration methods

S3.1 Isotopologue amount fraction calibration method
In this method the amount fraction of the isotopologues $^{12}$CH$_4$, $^{13}$CH$_4$ and $^{12}$CH$_3$D are calibrated individually, producing an estimate of the amount fraction of each in the sample. This follows the procedure described in Griffith et al.$^4$, where it was used for measurements of CO$_2$ isotope ratio with a Fourier transform infrared spectrometer.

The amount fraction of each isotopologue is not directly known for the PRMs, instead these are calculated from the gravimetric amount fraction and the assigned $\delta^{13}$C and $\delta^2$H. The mole fraction is the amount of an isotopologue relative to all CH$_4$ isotopologues in a sample, i.e. it is a fraction where the value for all isotopologues sums to one and depends only on the isotopic signature. We consider the three main CH$_4$ isotopologues $^{12}$CH$_4$, $^{13}$CH$_4$ and $^{12}$CH$_3$D and assume a statistical distribution of isotopes – i.e. no clumping. The ratio of minor to major isotope and is

$$r = \frac{13C}{12C}$$

$$r = \frac{D}{H}$$

calculated by rearranging equation (1) from the main text:

$$13r = 13r_{ref}(1 + \delta^{13}C)$$

$$2r = 2r_{ref}(1 + \delta^2H)$$

(S1)

Where $13r_{ref} = 0.01118$ and $2r_{ref} = 0.00015575$ are the reference ratios for $^{13}$C/$^{12}$C and D/H respectively (based on the VPDB and VSMOW scales). The mole fraction of the three isotopologues is given by

$$X_{211} = \frac{1}{R_{sum}}$$

$$X_{311} = \frac{13r}{R_{sum}}$$

$$X_{212} = \frac{42r}{R_{sum}}$$

(S2)

with $R_{sum} = (1 + 13r)(1 + 2r)^4$.

Assuming no fractionation during gravimetric dilution in CH$_4$-free diluent the isotopologue amount fraction for the PRMs is then the gravimetric total CH$_4$ value multiplied by the mole fraction. The line strengths used by the spectrometer to fit the spectrum are taken from the Hitran2016 database and are weighted by the natural terrestrial isotopic abundances$^1$. Therefore, the isotopologue amount fractions for the PRMs are therefore also scaled using the reference ratios $^{13}r_{hitran} = 0.0112374$ and $^{2}r_{hitran} = 0.000156$ to calculate a mole fraction scaling factor using equation (S2).

The uncalibrated instrument response varies linearly with the amount fraction for each isotopologue separately:

$$I_{211} = a_{211} Y_{211} + b_{211}$$

(S3)

$$I_{311} = a_{311} Y_{311} + b_{311}$$

(S4)

$$I_{212} = a_{212} Y_{212} + b_{212}$$

(S5)

The calibration values $a_i$ and $b_i$ are determined for each isotopologue using the calibration PRMs, CS-L and CS-H, and are recalculated for each cycle of the instrument. These values show drift between runs, which we account for by linearly interpolating values for $a_i$ and $b_i$ over time.
The spectrometer response – either for the calibration target PRM (CT), spectrometer target PRM (ST), or processed air sample – is calibrated to an amount fraction for each isotopologue using \( a_i \) and \( b_i \), then the ratio of rare to common isotopologue calculated and expressed in delta notation.

\[
\delta^{13}C = \frac{(Y_{311}/Y_{211})^{13}_{\text{Hitran}}}{(Y_{211}/Y_{211})^{13}_{\text{VPDB}}} - 1
\]  

(S6)

\[
\delta^2H = \frac{(Y_{212}/Y_{211})^{2}_{\text{Hitran}}}{(Y_{212}/Y_{211})^{2}_{\text{VSMOW}}} - 1
\]  

(S7)

The ratios \( ^{13}r_{\text{Hitran}} \) and \( ^{2}r_{\text{Hitran}} \) are included to account for the weighting carried through in the isotopologue calibration.

**S3.2 Isotope Ratio Calibration**

The ratio of uncalibrated instrument response to the rare and common isotopologues is taken directly without further processing and this ratio calibrated with respect to a known reference. A second step of correction is then required to account for the variation with amount fraction.

The rare-to-common isotope ratio for the sample is compared to CS-L, similar to the comparison to a scale standard such as VPDB in equation (1) in the main text. The isotope ratio for CS-L is given relative to the international scale as \( \delta_{\text{std}}^{13}C(CH_4) \) and is used to transfer measurements onto the same scale:

\[
r^{\text{VPDB}}_{\text{std}} = \frac{r_{\text{std}}}{\delta_{\text{std}}^{13}C + 1}
\]  

(S8)

where \( r_{\text{std}} = I_{311}^{\text{std}}/I_{211}^{\text{std}} \). The isotope ratio for a sample is then given on the same scale as the standard using this ratio as the reference:

\[
\delta^{13}C(\text{samp}) = \frac{r_{\text{samp}}}{r^{\text{VPDB}}_{\text{std}}} - 1
\]  

(S9)

In the case of optical absorption instruments, differences in the relative response to amount fraction for the individual isotopologues causes inaccuracy – a so called amount fraction, or mole fraction, dependence. This can be addressed with a phenomenological correction using a second standard mixture of the same \( \delta_{\text{std}}^{13}C \) and different amount fraction. Using the instrument response as the basis of this correction means that the amount fraction for this second standard also does not need to be known.

The response for CS-H is characterised by an instrumental isotope ratio using the ratio of responses for CS-H and CS-L:

\[
\delta_{\text{inst}}^{13}C(\text{high}) = \frac{r_{\text{high}}}{r_{\text{std}}} - 1
\]  

(S10)

With \( r_{\text{high}} = I_{311}^{\text{high}}/I_{211}^{\text{high}} \)

A correction factor \( m \) is calculated as a function of instrument response to all isotopologues \( l = I_{211} + I_{311} + I_{212} \):

\[
m = \frac{r_{\text{high}}}{r_{\text{std}}} - 1
\]
Finally, this correction is applied to the sample $\delta^{13}C(samp)$ from equation (S9)

$$\delta^{13}C(samp\text{- corrected}) = \delta^{13}C(samp) - m(I_{samp} - I_{std})$$  \hspace{1cm} (S12)
S4 Mass spectrometry measurements and scale linkage

Selected samples (Table 1) were analysed at Royal Holloway University of London (RHUL) for $\delta^{13}C$ using a modified GC-IRMS system (Trace Gas and 362 Isoprime mass spectrometer, Isoprime Ltd.) as described in detail by Fisher et al. Each cylinder was analysed 12 times over the course of nine days from 12th-21st October 2020. Measured values are given in Table 1 along with repeatability. The RHUL ambient air working standard is measured 3 times at the start of each day and then after every 2 samples to check for drift. The NPL samples were analysed on the same days as two ambient air secondary tanks, both provided by NOAA, one of which is analysed every week and the other every 4 weeks to check for long term drift and potential offsets that may result from changing He carrier gas or CO$_2$ reference cylinders, and a near annual replacement of the working standard. One of the NOAA tanks has an assigned $\delta^{13}C$ of CO$_2$ of -8.4‰. This is used to assign a value to each new reference CO$_2$ cylinder. A scale contraction correction is applied and then data intercompared with samples exchanged with INSTAAR (USA), NIWA (NZ) and IMAU (NL). A recent intercomparison for $\delta^{13}C$ with IMAU for the MEMO$^2$ project showed agreement over the range of -62 to -38‰ of better than ±0.1‰ for amount fractions between 2 µmol mol$^{-1}$ and 10 µmol mol$^{-1}$ CH$_4$.

We did not have access to IRMS analysis for $\delta^2H$ and were therefore unable to make the comparison against IRMS measurements as we have done for $\delta^{13}C$. We were, however, able to assign our measurements on the VSMOW international scale by using the atmospheric record from Mace Head that was created by NOAA-INSTAAR over the period 2005-2009. Based on this record we estimated a $\delta^2H$ of -92.63‰ for BT (representative of an unpolluted sample from Mace Head), which led to an estimated $\delta^2H$ for the calibration PRMs’s CH$_4$ of -192.70‰ (within the expected range for a fossil source of CH$_4$). The absolute value does not influence the analysis of instrument repeatability: Figure S3 shows that the calibrated value for BT varies in proportion to the assigned value for the calibration PRMs, however, the standard deviation of 116 measurements (1.32 ‰) is the same regardless of this assigned ratio.

![Figure S3](image-url)

**Figure S3** Calibrated isotope ratio $\delta^2H$ for the BT (y-axis) for different choices of the value assigned to the calibration PRMs (x-axis).
S5 Calculation of CH₄ amount fraction in ambient air

The amount fraction of CH₄ in the sample delivered to the spectrometer is higher than ambient air by a factor of >250. We determine the total CH₄ amount fraction in ambient air by reference to the assigned value of a whole-air working standard (in this case BT). This working standard is processed through the preconcentrator alternately with the air sample under nominally identical treatment, but differences between the regulator pressures or sample humidity cause variation in the trap flow rate and volume sampled. We therefore use a normalised instrument response \( I_{\text{norm}} \) from the ratio of the raw \(^{12}\text{CH}_4\) value reported by the spectrometer \( I_{211} \) to the volume of air sampled and measured \( V_{\text{trap}} \) from MFC-2 during trapping i.e. \( I_{\text{norm}} = I_{211}/V_{\text{trap}} \). This quantity is calculated for the air sample and the two standard measurements that bracket it in time. The \( I_{\text{norm}} \) for the two standards are linearly interpolated onto the timestamp of the air measurement so the relative response calculated for air is:

\[
R_L = \frac{I_{\text{norm}}(\text{air})}{I_{\text{norm}}(\text{standard, interp})}
\]

The amount fraction is then the relative response multiplied by the known amount fraction of CH₄ in the whole air working standard.
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