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

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## Abstract

We present a new instrument, 'Boreas', a cryogen-free methane ( $\text{CH}_4$ ) preconcentration system coupled to a dual laser spectrometer for making simultaneous measurements of  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^2\text{H}(\text{CH}_4)$  in ambient air. Excluding isotope ratio scale uncertainty, we estimate typical standard measurement uncertainty for an ambient air sample of 0.07 ‰ for  $\delta^{13}\text{C}(\text{CH}_4)$  and 0.9 ‰ for  $\delta^2\text{H}(\text{CH}_4)$ , which is the lowest reported for a laser spectroscopy-based system and comparable to isotope ratio mass spectrometry. We trap  $\text{CH}_4$  ( $\sim 1.9 \mu\text{mol mol}^{-1}$ ) from  $\sim 5 \text{ l}$  of air onto the front end of a packed column, subsequently separating  $\text{CH}_4$  from interferences using a controlled temperature ramp with nitrogen ( $\text{N}_2$ ) as the carrier gas, before eluting  $\text{CH}_4$  at  $\sim 550 \mu\text{mol mol}^{-1}$ . This processed sample is then delivered to an infrared laser spectrometer for measuring the amount fractions of  $^{12}\text{CH}_4$ ,  $^{13}\text{CH}_4$  and  $^{12}\text{CH}_3\text{D}$  isotopologues. We calibrate the instrument using a set of gravimetrically prepared amount fraction primary reference materials directly into the laser spectrometer that span a range of  $500 \mu\text{mol mol}^{-1}$  to  $626 \mu\text{mol mol}^{-1}$  ( $\text{CH}_4$  in  $\text{N}_2$ ) made from a single pure  $\text{CH}_4$  source that has been isotopically characterised for  $\delta^{13}\text{C}(\text{CH}_4)$  by IRMS. Under the principle of identical treatment a compressed ambient air sample is used as a working standard and measured between air samples, from which a final calibrated isotope ratio is calculated. Finally, we make automated measurements of both  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^2\text{H}(\text{CH}_4)$  in over 200 ambient air samples and demonstrate the application of Boreas for deployment to atmospheric monitoring sites.

## Introduction

Methane ( $\text{CH}_4$ ) concentrations have more than doubled over the last 150 years, and the contribution to increased radiative forcing since the industrial revolution is around a quarter of

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3 that relative to carbon dioxide (CO<sub>2</sub>)<sup>1</sup>. Mitigation of CH<sub>4</sub> emissions therefore plays a vital role  
4 in tackling the climate crisis. Unlike CO<sub>2</sub> that has shown a very consistent rise in the  
5 atmosphere over the last century, owing to anthropogenic fossil fuel emissions, CH<sub>4</sub> has gone  
6 through periods of small changes in the growth rate for reasons that are poorly understood<sup>2</sup>.  
7 Methane is emitted from a variety of sources and processes, and largely removed by chemical  
8 destruction in the troposphere (global atmospheric lifetime of ~decade). Although  
9 anthropogenic emissions have been a clear main driver of the rising global atmospheric  
10 concentrations over the last century, the sectoral (e.g. agricultural versus energy), temporal and  
11 spatial disaggregation of emissions remains poorly quantified and difficult to verify through  
12 atmospheric measurements of amount fractions alone<sup>3</sup>. While the main thrust of the widespread  
13 mitigation measures needed is very clear (eliminate fugitive leaks during fossil fuel extraction  
14 and transport and develop low-emission agricultural methods) the measurement tools to aid  
15 timely, efficient and equitable policy decision making are lacking<sup>3</sup>.  
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21 Different formation, transport, and removal processes can impart distinctive isotopic  
22 fractionations on molecules<sup>4</sup>. These naturally-occurring isotopic labels provide an extra layer  
23 of information for studying biogeochemical cycling and anthropogenic emissions<sup>3, 5</sup>. Isotopic  
24 composition, typically measured by isotope ratio mass spectrometry (IRMS), has provided key  
25 insights into our understanding of the historical and contemporary global atmospheric budgets<sup>5</sup>.  
26 Isotopic records are largely constructed by continuous or one-off sampling campaigns followed  
27 by analysis in the laboratory by isotope ratio mass spectrometry<sup>6</sup>. The high-quality  
28 measurements needed for such studies are difficult to make, time consuming and expensive,  
29 and only performed by fewer than 20 laboratories across the world<sup>7</sup>. In populated regions, such  
30 as Europe, different types of emission sources are in proximity, making it difficult to usefully  
31 verify emissions (i.e. quantitatively separate different sources) using atmospheric  
32 measurements. However, in bringing together the source-specific information gained from  
33 isotopic observables and the benefits of coupling high-frequency measurements with high-  
34 resolution atmospheric chemistry transport model (ACTM) outputs, we will be able to make a  
35 significant improvement in our quantitative understanding of sector-specific fluxes<sup>8-9</sup>. To this  
36 end, impressive attempts have been made to take IRMS systems to atmospheric observatories  
37 for high precision, in situ, frequent analysis of both  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^2\text{H}(\text{CH}_4)$ <sup>9-11</sup>. These studies  
38 generated thousands of measurements over many months providing data that could be  
39 assimilated into ACTMs for interpretation.  
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45 Instruments (such as Fourier transform infrared or laser absorption spectrometers) can make  
46 high-frequency measurements with potentially lower maintenance requirements, therefore  
47 allowing atmospheric monitoring at greater spatial coverage. However, commercial  
48 spectrometers are unable to make sufficiently high-precision  $\delta^{13}\text{C}(\text{CH}_4)$  and  $\delta^2\text{H}(\text{CH}_4)$   
49 measurements due to the low abundance of CH<sub>4</sub> in ambient air, which results in a poor signal-  
50 to-noise ratio (currently dry air amount fractions in the well-mixed atmosphere are < 2  $\mu\text{mol}$   
51  $\text{mol}^{-1}$ ). One method to improve the signal-to-noise ratio is to concentrate the analyte of interest  
52 out of ambient air for analysis with a commercially-available spectrometer. Eyer et al.<sup>12</sup> made  
53 progress in developing this approach for simultaneous measurements of  $\delta^{13}\text{C}(\text{CH}_4)$  and  
54  $\delta^2\text{H}(\text{CH}_4)$  by laser spectroscopy, and later showed the potential for these more efficient  
55 measurement systems to be deployed<sup>9</sup>. The measurement repeatability (0.19‰ for  $\delta^{13}\text{C}$  and  
56 1.9‰ for  $\delta^2\text{H}$ ), however, was significantly larger than those of laboratory-based IRMS methods  
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( $<0.05\%$  for  $\delta^{13}\text{C}$  and  $1\%$  for  $\delta^2\text{H}$ ). This study also highlighted significant problems for analysis that included the potential for breakthrough on traps (due to the large sample volume needed), and the issue of variable oxygen ( $\text{O}_2$ ) content of the trapped sample that continues on to create a matrix effect in analysis by laser spectroscopy.

In this work we describe the design of a new robust preconcentration system coupled to a dual-laser spectrometer and demonstrate several weeks of continuous operation alternating between ambient air samples and whole-air reference standards. Alongside this we describe a rigorous and efficient calibration procedure for isotopologue ratio measurements from ambient air samples – the first demonstration of an isotopologue amount fraction-based calibration scheme for  $\text{CH}_4$  using synthetic gravimetrically-prepared standards.

## Methods

### Overview

The limitations to using infrared laser absorption spectroscopy for isotope ratio measurement of atmospheric  $\text{CH}_4$  arise from the weak signals due to low ambient amount fractions and interference from other gases. Boreas tackles this problem by physically separating interferences while increasing the amount fraction in the sample that is then introduced into the spectrometer.

Boreas is constructed from three distinct connected parts: 1) a purpose-built unit for sampling,  $\text{CH}_4$  preconcentration and interference removal; 2) a sampling interface to prepare the gas sample for the spectrometer; and 3) a mid-infrared dual-laser spectrometer. Calibration of the spectrometer is performed separately with amount fraction primary reference materials (AF PRMs) of  $\text{CH}_4$  in nitrogen ( $\text{N}_2$ ). Whole-air target gas working standards are treated the same as an air sample and used to perform a final correction to the spectrometer-only calibration. The system is fully automated and alarmed, allowing continuous remote operation for weeks with high purity  $\text{N}_2$  carrier gas and standard gases as the only consumables.

### Instrument description

#### Laser spectrometer

The spectrometer is a commercial high-resolution dual-laser direct absorption instrument (Aerodyne Research, Inc, TILDAS-FD-L2). The wavelength of a pair of quantum cascade lasers is swept sequentially over two frequency ranges:  $1299.703\text{ cm}^{-1}$  to  $1293.816\text{ cm}^{-1}$  for  $^{12}\text{CH}_4$  and  $^{13}\text{CH}_4$  and  $1306.883\text{ cm}^{-1}$  to  $1307.077\text{ cm}^{-1}$  for  $^{12}\text{CH}_4$  and  $^{12}\text{CH}_3\text{D}$ . The resulting spectrum is fitted for the amount fraction of the isotopologues using parameters from the Hitran2016 database<sup>13</sup>, and a polynomial baseline. Details are given in the supporting information S1.

#### Sampling and preconcentration

The sampling and preconcentration unit was custom-built at the National Physical Laboratory (NPL), UK. A schematic of the sample flow scheme is shown in Figure 1. The core piece of hardware is a cryo-cooler (CryoTel GT Sunpower Inc., USA) that is able to reach temperatures of  $< 40\text{ K}$  with minimal heat load, and at  $100\text{ K}$  has a lift of  $> 20\text{ W}$ . The cold end of this cryo-cooler is housed in a vacuum for thermal isolation (below  $10^{-6}\text{ mbar}$  pumped by an Edwards nEXT85D turbomolecular pumping station), interfaced with the sample gas via a trap tube (stainless steel,  $1.5\text{ m}$  long,  $1/8''$  outside diameter,  $2.0\text{ mm}$  inside diameter) containing

HayeSep-D (1 m packed length of 100/120 mesh) with a 250 mm void at each end (Thames Restek UK Ltd). Thus, the volume of 100/120 mesh HayeSepD is calculated as 3142 mm<sup>3</sup>, which is comparable to other systems such as the Medusa GC-MS and TREX which have trapping volumes of 1544 mm<sup>3</sup> and 6363 mm<sup>3</sup>, respectively<sup>12, 14-15</sup>. The trap tube is wrapped around a cylindrical standoff permanently attached to the cold end of the cryocooler in a manner similar to previous designs<sup>14-16</sup>, and heated resistively via a custom-built variable-voltage power supply unit. The temperature of the trap is monitored using a pair of thermocouples (TCs) affixed to both the trap tubing and the inside of the standoff. Valves 1-6 are VICI Valco GC valves with electronic actuators: Valves 1 and 6 are 6-port multi-selector models (VIEUTA-2LCSD6UWEPH) for connection of Boreas and Aerodyne sample and standard gases, respectively. Valves 2, 4 and 5 are 4-port 2-position models (VIEUDA-2C4UWEPH), valve 3 is a 6-port valve with a special rotor engraving and a 12-position motor that can direct the gas during the sampling sequence between the sample, trap, N<sub>2</sub> flush and the spectrometer (VIEUDA-2C6UWEPH-SI2). Valve 4 controls the flow direction through the trap, and valve 5 acts to isolate the trap from the rest of the gas manifold. Flow rates are controlled by mass flow controllers (MFCs) 1 to 3 (Red-Y, GSC-B3SA-BB22). The pressure drop across the trap is monitored by two absolute pressure transducers (Sensors One, DTC 531).

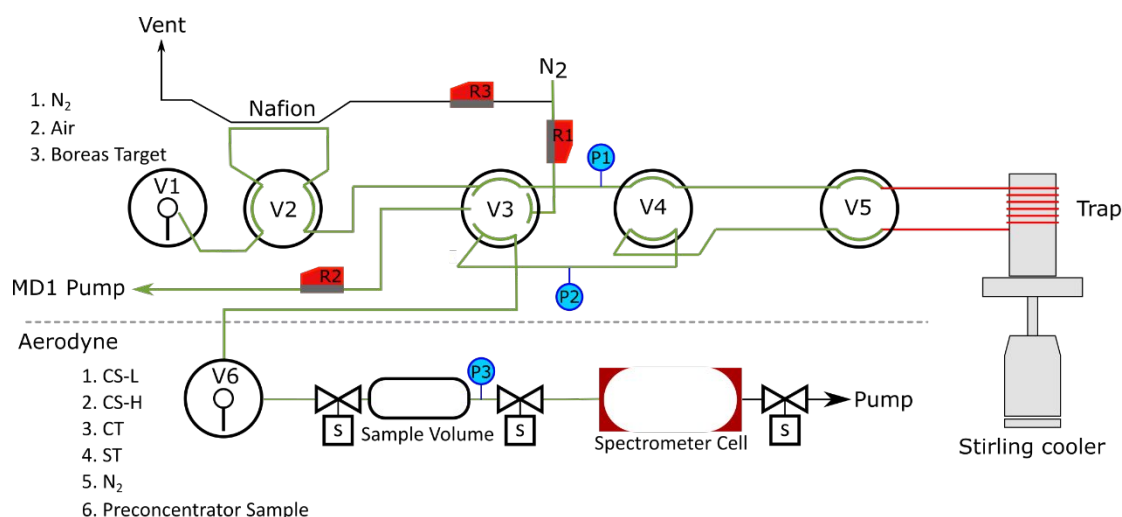


Figure 1 Flow scheme for the sampling of CH<sub>4</sub> from ambient air and delivery to the laser spectrometer. Valves 1-6 (V1-V6), mass flow controllers (R1-R3) and the pressure transducers (P1-P3) are labelled. The solenoid valves are denoted by the squared "S". The sampling volume and spectrometer cell are notated in the figure. Multi-selector V1 has 3 ports connected; (1) N<sub>2</sub>; (2) air; and (3) the Boreas Target (BT). Multi-selector V6 has 6 ports connected that lead to the spectrometer; (1) low calibration standard AF PRM (CS-L); (2) high calibration standard AF PRM (CS-H); (3) calibration target AF PRM (CT); (4) spectrometer target AF PRM (ST); (5) pure N<sub>2</sub>; and (6) sample from the trap. The dotted line indicates the separation of control between the preconcentrator and the spectrometer software.

The timing of events in a single sampling cycle is shown in Figure 2 and consists of four phases;— trapping, CH<sub>4</sub> separation, CH<sub>4</sub> elution and trap reconditioning, before the trap is allowed to cool for the next cycle.

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*(a) Trapping (0 s to 660 s)*

The ambient air sample is brought to the head of the trap using a sampling pump (N143 Series, KNF Neuberger UK Ltd, UK) with an outlet pressure of 4.5 bar, controlled by a backpressure regulator, creating a flow rate downstream of the trap measured by MFC-2 of  $\sim 580 \text{ ml min}^{-1}$  (STP); the pressure of the whole-air standard is set by a cylinder-mounted regulator. The sample gas is dried by a Nafion dryer with a  $\text{N}_2$  (Air Products, BIP purity) counter-purge at a flow rate of  $200 \text{ ml min}^{-1}$  during sampling and  $20 \text{ ml min}^{-1}$  when not sampling, set by MFC-3. Valve 4 is set to forward-flow the sample through the trap and V3 is set to direct the effluent to vent through R2 (this also isolates V6 and the spectrometer from the preconcentrator). V5 is initially set so the flow bypasses the trap, allowing the rest of the system to purge with the sample. After two minutes of flow to purge the valve system the bypass valve V5 opens to the trap, which can be seen as the step change in flow and pressure at the start of phase (a) in Figure 2. The sample flows through the trap starting at  $\sim 113 \text{ K}$  without any active heating but while the trap is still cooling from the previous run. Trapping continues for 540 s during which the trap cools a further 10 K to 103 K at the end of trapping. The trapping temperature does not need to be controlled by any active heating (trapping temperature repeatability between cycles is  $< 1 \text{ K}$ ). Trace gases from around  $\sim 5 \text{ l}$  of air (STP) are trapped on the adsorbent by the end of sampling, the integrated volume is recorded for each run from the flow measured by MFC-2.

During phases (a) and (b) the spectrometer is successively filled with four of the high amount fraction mixtures, and the spectra recorded for 100 s. These gases flow through the sampling volume in order to match the pressure of the trap sample and this can be seen as the spikes of pressure in the sampling volume plotted in blue in Figure 2.

*(b) Methane separation (660 s to 900 s)*

After 540 s sampling is discontinued by moving the sample selector V1 to a blanked inlet and letting the trap decompress by pumping out through MFC-2 for 240 s. This decompression reduces the dead volume of gas in the system and the trap and limits the backward expansion of the sample at the onset of heating. At 900 s the trap is heated from 103 K to 373 K over 720 s. During this period the trap is forward flushed (still to vent through MFC-2) at a flow rate of  $6 \text{ ml min}^{-1}$  and then  $10 \text{ ml min}^{-1}$  with  $\text{N}_2$  (controlled by MFC-1) as the resistance of the trap to flow increases with temperature.

*(c) Methane elution (1260 s to 1410 s)*

At  $\sim 360 \text{ s}$  into the temperature ramp V3 steps position to divert the trap effluent to a 50 ml sampling volume (Swagelok stainless steel miniature sample cylinder). Once the pressure reaches 375 mbar the sampling volume is shut off. This filling can be seen as the rising pressure in the sampling volume during phase (c) plotted as a blue line in Figure 2. The exact timing of the valve steps is optimised to capture all eluted  $\text{CH}_4$  into the sampling volume, using the procedure described below.

*(d) Reconditioning 1620 s to 1950 s)*

At the end of the  $\text{CH}_4$  elution step V3 steps to the third position, and the trap effluent returns to vent. At this point the trap has reached over 273 K and the ramp continues to 373 K and is

maintained for 300 s while the trap is reconditioned by the purging of less volatile species (most significantly H<sub>2</sub>O). The heating is then cut off and the trap allowed to cool passively via the dissipation of heat through the cryocooler.

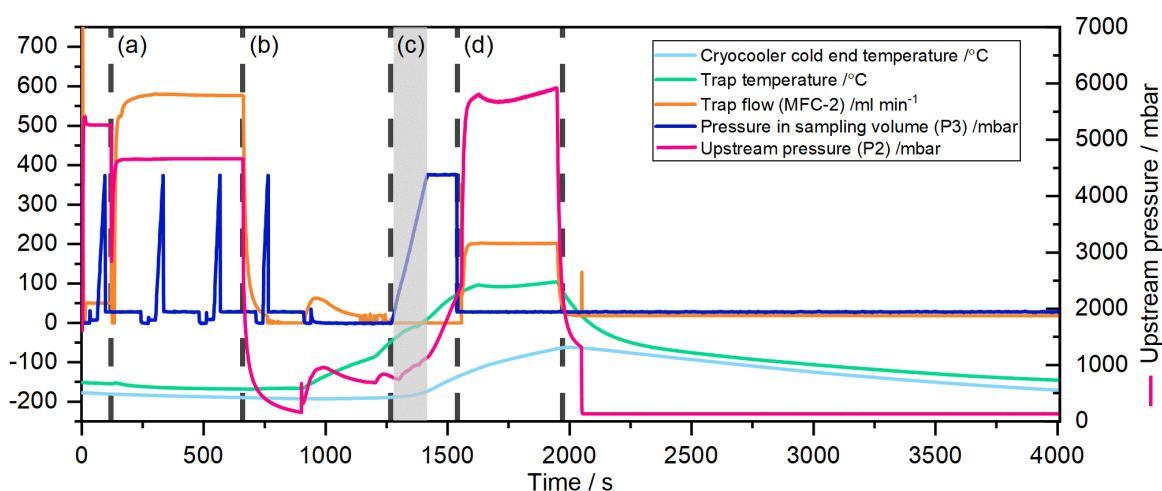


Figure 2 Stripchart of various instrument parameters during a run. Top (left axis): Cryocooler cold end temperature; trap temperature (thermocouple attached midway on outside of the trap tubing); trap flow (recorded by the mass-flow controller down-stream of the trap); sampling volume pressure (Figure 1, P3): The sampling volume pressure's four peaks between 0 and 750 s are loading of the standards, independent of the preconcentrator operation. Right axis: upstream pressure (Figure 1, P2). Vertical dashed lines mark the boundaries of each phase (a) trapping (b) CH<sub>4</sub> separation (c) CH<sub>4</sub> elution (d) reconditioning.

### The sampling-spectrometer interface and instrument control

The sampling system is fully automated and controlled using GCWerks (GCSoft Inc) on a Linux-based computer. Once the CH<sub>4</sub> has been transferred into the sampling volume, control passes to the laser spectrometer software, TDLWintel (Aerodyne Research Inc) and the gas mixture in the sampling volume is equilibrated with the 500 ml cell (previously evacuated) within the laser spectrometer for measurement of the three isotopologue abundances. On completion of the measurement (see section 3.1 below) the sampling volume and cell are evacuated in preparation for calibration of the instrument using the synthetic standard gases (see section 3.3 below).

Each sample from an AF PRM or from the trap is loaded into the spectrometer and is automatically analysed by the spectrometer software. The trap eluent contains varying amounts and possibly different isotopic compositions of CH<sub>4</sub> (see period c in Figure 2), along with other gases that are being removed from the trap at the same time (see section 3.2), so the mixture is allowed to homogenise in the sample volume for two minutes. The preconcentrated sample or AF PRM sample are first loaded into the sample volume at 375 mbar. The solenoid valve downstream of the sampling volume then opens allowing the mixture to expand into the spectrometer cell to a final pressure of 28.5 mbar.

## Measurement protocols and calibration methodology

### Laser spectrometer measurement acquisition

Once in the laser spectrometer cell the mixture is given 30 s to equilibrate thermally, during which the instrument response changes as the gas warms to the cell temperature. After equilibration the spectrum is recorded at 1-second intervals and each spectrum is fitted for an

amount fraction. This gives 100 seconds of reported amount fraction data which are then averaged to give the measurement for each sample. This optimum averaging time was determined from the minimum in the Allan variance, which indicates the period dominated by random noise before systematic drift starts to influence the result. Details of the spectrometer stability and optimum averaging time are given in the supporting information S2.

### Optimisation of CH<sub>4</sub> elution from the trap

Quantitative capture of CH<sub>4</sub> from the trap is essential in order to prevent isotopic fractionation while preventing co-elution of possible spectroscopic interfering analytes that can vary in amount in ambient air (e.g. nitrous oxide, N<sub>2</sub>O). To this end, we also use the HaysepD trap as a chromatographic column by fore-flushing CH<sub>4</sub>. This allows volatile gases such as O<sub>2</sub> to be largely removed before elution of CH<sub>4</sub>, while variable and less volatile gases such as N<sub>2</sub>O remain on the trap until later in the temperature ramp. We optimised the system by sampling the trap eluent at different transfer time delays with respect to the start of the temperature ramp 10 s apart in a set of otherwise identical runs. This is necessary in our system (closed spectrometer vs flow through) whereby the elution profiles of analytes cannot be measured directly in real time. The sample volume fills to the same 375 mbar pressure in each of these runs with the flushing N<sub>2</sub>. The CH<sub>4</sub> amount fraction as a function of time delay effectively shows the time profile for CH<sub>4</sub> elution, but the shape of this peak is broadened by the approximately 100 s that the valve is opened. We perform a simple deconvolution of this “instrument function” to recover an estimate of the elution profile by taking the difference between the CH<sub>4</sub> amount fraction from two consecutive runs and dividing this by the difference in transfer time delay between the runs (10 s). Figure 3 plots this estimate for the CH<sub>4</sub> and N<sub>2</sub>O spectrometer signals for a set of different transfer time delays. This demonstrates that the chosen transfer delay time and duration (represented by the gray shading) completely encloses the CH<sub>4</sub> elution profile and that there is significant separation (~90 s) between the end of CH<sub>4</sub> elution and the start of N<sub>2</sub>O, allowing the sampling volume to be closed off before N<sub>2</sub>O elution.

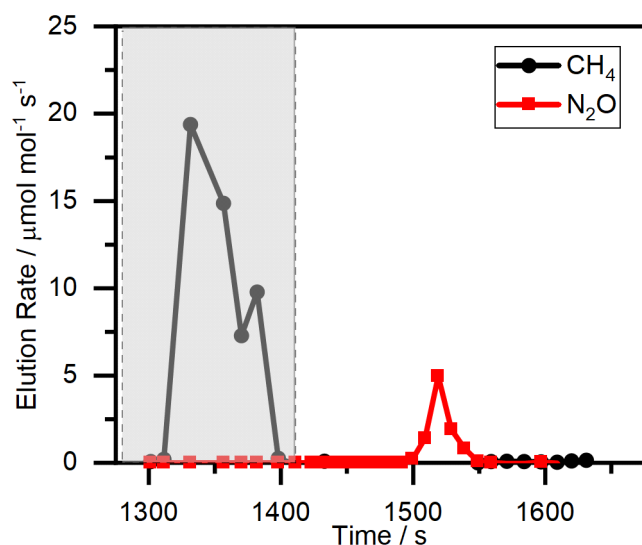


Figure 3 Elution profile of CH<sub>4</sub> and N<sub>2</sub>O from the trap, reconstructed by a deconvolution procedure described in the text. Each point is a separate instrument cycle and the spectrometer measures CH<sub>4</sub> and N<sub>2</sub>O simultaneously for each sample. The time axis is the relative to the start of the cycle (Figure



2) and the shaded region indicates the valve timing selected as the optimum during which the sample volume is filled.

We analysed the composition of the Boreas trap eluent (collected under optimised conditions) for other major gases that were concentrated and eluted together with CH<sub>4</sub> but are not visible to the laser spectrometer. The preconcentrator was allowed to sample from the Boreas target whole air standard (Table 1), however, instead of transferring to the sampling volume for equilibration and injection into the spectrometer, the trap eluent was captured into a different 50 ml gas cylinder fitted with a valve for removal and offline analysis. The eluant has a nominal composition of approximately 550 μmol mol<sup>-1</sup> CH<sub>4</sub> in the pure N<sub>2</sub> carrier gas plus trace amounts of other air components more volatile than CH<sub>4</sub> such as O<sub>2</sub>, argon (Ar) and krypton (Kr). This eluant was transferred to an evacuated 10 L (water volume) gas cylinder and diluted in helium (He) (Air Products, BIP) to pressurise the mixture for analysis by gas chromatography. The dilution factor from He addition is estimated as 0.02% from the accurate mass of each addition determined by gravimetry and assuming the eluant is pure N<sub>2</sub> for the purpose of estimating molecular mass. The permanent gas components were separated using two capillary columns (2 x molsieve 5A, 30 m x 0.53 mm x 0.50 μm) and detection was on a pulsed-discharge He ionisation detector (PDHID). By comparison with NPL in house standards, the amount fraction of O<sub>2</sub> in the sample was calculated as (10 ± 1) mmol mol<sup>-1</sup>. The concentrations of other permanent gases (Kr and Ar) in the sample were < 0.5 mmol mol<sup>-1</sup>.

### Isotope Ratio Calibration

The accuracy of molecular spectroscopy measurements made by a laser spectrometer depends on either the excellent characterisation of the matrix effect (line broadening etc) or on preparation of standards that contain the same matrix and interfering components as the sample of interest. Differences in the composition of both the calibration gases and sample lead to differences in the instrument response that will create a bias in the calibrated amount fraction. The process of concentrating CH<sub>4</sub> necessarily leads to alteration of the ambient air matrix i.e. the proportion of O<sub>2</sub> to N<sub>2</sub> and noble gases. We therefore aimed to concentrate CH<sub>4</sub> from air on the trap and then remove the CH<sub>4</sub> from the trap with pure N<sub>2</sub> carrier gas..

This approach has significant potential for developing a long term, simplified and traceable calibration strategy: if the CH<sub>4</sub> from air can be transferred to a pure-N<sub>2</sub> matrix (i.e. the preconcentrator both boosts the sensitivity of the spectrometer and removes pressure-broadening interferences), then synthetic AF PRMs alone can be used to calibrate Boreas. This approach lends itself particularly well to calibration of a laser spectrometer. In theory, the spectrometer can be calibrated using only a set of standards with different well-known amount fractions but with identical isotopic composition. So long as the linearity of the instrument is well characterised, memory effects in the instrument are negligible, and the calibration gases hold the same matrix as the sample, then an accurate isotope ratio measurement can be made<sup>17-18</sup>.

### Calibration standards and targets

Two high AF PRMs prepared from CH<sub>4</sub> in N<sub>2</sub> were used as calibration standards for the spectrometer by directly filling the cell: calibration standard low, calibration standard high (CS-L, CS-H). Two more high AF PRMs are used to validate the spectrometer calibration: one named calibration target (CT) containing CH<sub>4</sub> from the same source as CS-L and CS-H,

and one named spectrometer target (ST) containing CH<sub>4</sub> from a different parent batch. Two compressed whole air samples (BT, H-354) were used to calibrate and characterise Boreas's performance by sampling through the preconcentrator. Two other AF PRMs for analysis by IRMS were prepared, with a CH<sub>4</sub> amount fraction near ambient, by diluting the CT and ST by further addition of N<sub>2</sub>.

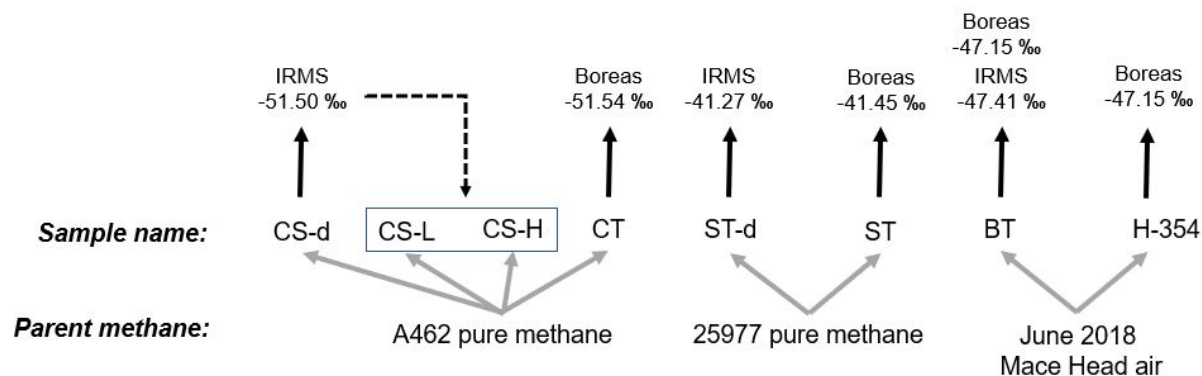


Figure 4 Schematic of the relationship between parent CH<sub>4</sub>, AF PRMs, whole air standards, and measurements made for  $\delta^{13}\text{C}$ . Grey arrows represent physical dilution of the parent CH<sub>4</sub> for preparation of the AF PRMs. All Boreas measurements shown here are made using calibration of the spectrometer via two synthetic mixtures CS-L and CS-H with 500  $\mu\text{mol mol}^{-1}$  and 626  $\mu\text{mol mol}^{-1}$  amount fractions in N<sub>2</sub>, respectively.

Table 1 provides a full list of samples and mixtures together with sample name and description, and Figure 4 shows the relationship between the parent CH<sub>4</sub> source and the mixtures prepared for measurement by Boreas and IRMS. The AF PRM calibration standards (CS-L, CS-H) and calibration target (CT) were prepared gravimetrically by diluting a 2.23% CH<sub>4</sub> (N6.0, CK gases) parent standard to 500  $\mu\text{mol mol}^{-1}$ , 626  $\mu\text{mol mol}^{-1}$  and 550  $\mu\text{mol mol}^{-1}$ , using high-purity N<sub>2</sub> (N6.8 grade BIP+, Air Products). The CH<sub>4</sub> for ST came from another source (25977 technical grade 2.5, Air Products) diluted to 600  $\mu\text{mol mol}^{-1}$  using the same high-purity N<sub>2</sub>. These synthetic AF PRMs allowed us to calibrate and assess the performance of the spectrometer alone, and BT and H-354 are used to characterise the performance of the full Boreas system. These cylinders (50 l water volume, aluminium Luxfer gas cylinders, Matar, Italy) were filled at the Mace Head Observatory using an oil-free compressor (RIX Industries) following National Oceanographic and Atmospheric Administration (NOAA) procedures for certified reference materials involving processes of cylinder conditioning and venting before a final fill to  $\sim 200$  bar<sup>19</sup>. The cylinders were filled under conditions of atmospheric transport from the Atlantic that were representative of the well mixed high latitudes of the Northern Hemisphere.

**Table 1** The prepared gas standards (AF PRMs and whole air) used to calibrate and characterise the performance of Boreas. The rows with a grey background denote mixtures prepared gravimetrically from one of the two pure CH<sub>4</sub> parents. The calibration standard CS-d was measured for δ<sup>13</sup>C by IRMS and this value assigned to the AF PRMs prepared from the same parent. Values without an uncertainty represent assigned δ<sup>13</sup>C based on measurements by IRMS, or for δ<sup>2</sup>H based on the scale anchor point from BT as described in supporting information S4.

Sample name (NPL ID)	CH <sub>4</sub> origin (NPL ID)	Description	CH <sub>4</sub> (μmol mol <sup>-1</sup> )	NPL Boreas		Externally measured or assigned values		
				δ <sup>13</sup> C (1SD, n) (‰)	δ <sup>2</sup> H (1SD, n) (‰)	δ <sup>13</sup> C (1SD, n) (‰)	δ <sup>2</sup> H (1SD) (‰)	δ <sup>13</sup> C Boreas offset (‰)
CS-L (NPL-2635)	CK gases (A462)	Low calibration standard AF PRM	500.1	n/a	n/a	-51.50	-192.70	n/a
CT (NPL-A662)	CK gases (A462)	Calibration target AF PRM	549.9	-51.54 (0.06, 116)	-192.66 (0.29, 116)	-51.50	-192.70	n/a
CS-H (NPL-A659)	CK gases (A462)	High calibration standard AF PRM	625.5	n/a	n/a	-51.50	-192.70	n/a
ST (NPL-2833)	Air Products (25977)	Spectrometer target AF PRM	599.9	-41.45 (0.06, 116)	-190.46 (0.29, 116)	-41.27	n/m	0.18
ST-d (NPL-3059)	Air Products (25977)	Near-ambient spectrometer target AF PRM for IRMS analysis	2.490	n/m	n/m	-41.27 (0.06, 12)	n/m	n/a
CS-d (NPL-2550)	CK gases (A462)	Near-ambient calibration AF PRM for IRMS analysis	2.006	n/m	n/m	<b>-51.50 (0.04, 12)</b>	<b>-192.70</b>	<b>Zero (anchor point)</b>
BT (H-356)	Ambient air (Mace Head filled June 2018)	Whole-air Boreas target	1.908	-47.15 (0.08, 58)	-92.63 (1.32, 58)	n/m	-92.63	n/m
H-354	Ambient air (Mace Head filled June 2018)	Whole-air IRMS/Boreas intercomparison sample	1.916	-47.15 (0.06, 26)	-94.79 (0.84, 25)	-47.41 (0.04, 12)	n/m	0.26

Where an uncertainty is provided it indicates a δ<sup>13</sup>C direct measurement of that sample either by IRMS (measured by RHUL as described in supporting information S4) or by Boreas (using the isotope ratio anchor points of NPL-2550 and as described in section 3.3).

n/a = not applicable as CS-H and CS-L are not measured by Boreas but used as the ‘known’ calibration standards with assigned isotope ratios

n/m = not measured

A sample of each pure CH<sub>4</sub> parent, diluted to near-ambient amount fraction in N<sub>2</sub> (CS-d and ST-d), and the whole-air standard BT were analysed at Royal Holloway University of London (RHUL) for δ<sup>13</sup>C, as described in the supporting information S4. δ<sup>13</sup>C has been assigned for the calibration standards by IRMS measurement, however δ<sup>2</sup>H has not been directly measured. We estimate an assignment for δ<sup>2</sup>H by reference of the whole-air standard to the Northern Hemisphere background value, described in supporting information S4.

### Isotope ratio definition and notation

The isotope ratio applied to molecular species quantifies the proportion of molecules containing the rare isotope relative to the most abundant and this is expressed relative to the same ratio for a reference material

$$\delta^{13}\text{C} = \frac{Y_{311}/Y_{211}}{R_{\text{VPDB}}} - 1 \quad (1)$$

$$\delta^2\text{H} = \frac{Y_{212}/Y_{211}}{R_{\text{VSMOW}}} - 1 \quad (2)$$

where  $Y_{211} \equiv Y(^{12}\text{CH}_4)$ ,  $Y_{311} \equiv Y(^{13}\text{CH}_4)$  and  $Y_{212} \equiv Y(^{12}\text{CH}_3\text{D})$  are the calibrated amount fractions of <sup>13</sup>CH<sub>4</sub>, <sup>12</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>3</sub>D, respectively (following the notation in Griffith<sup>17</sup> and IUPAC where the symbol  $X_i$  is used for the mole fraction of isotopologue  $i$  – the proportion relative to all isotopologues – and  $Y_i$  for the amount fraction of the isotopologue – the proportion relative to the gas mixture composition; and the Air Force Geophysics Laboratory, AFGL, shorthand notation for isotopologues). Isotope ratios assigned by IRMS are the bulk values, i.e. the ratio for all carbon or hydrogen in the sample. The spectrometer measures isotopologues separately, so here the ratios are referenced to these specific molecules and neglect non-stochastic partitioning of isotopes among the ten stable isotopologues of CH<sub>4</sub>. Recently there has been significant developments in ‘clumped’ isotopic CH<sub>4</sub> geochemistry and it is likely that any difference between bulk isotope ratios and isotopologue ratios is below the experimental uncertainty of our measurements<sup>20</sup>. For conciseness we keep the notation δ<sup>13</sup>C to refer to δ<sup>13</sup>C (CH<sub>4</sub>), and δ<sup>2</sup>H to refer to δ<sup>2</sup>H(CH<sub>4</sub>), when discussing results.

### Calibration method

There are two approaches to calibrating an instrument response to produce a calibrated isotope ratio, for example δ<sup>13</sup>C relative to the VPDB scale, that relates to the order of operations. The first method is to calibrate the measured isotopologue amount fraction of <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> using amount fraction standards, then calculate the ratio of these quantities by equation (1); this is termed the isotopologue method here. The second method is to calculate the ratio of instrument responses <sup>13</sup>CH<sub>4</sub> to <sup>12</sup>CH<sub>4</sub> (i.e.  $r = I_{311}/I_{211}$ ) then calibrate this ratio using an isotopic standard (here termed the ratio method).

In IRMS, first calculating the ratio of instrument responses to <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> reduces common-mode noise in the measurement, most notably the mass-dependent isotopic fractionation effects due to incomplete transmission of ions through the mass spectrometer. Laser spectrometers, however, make independent absolute measurements of the amount fraction of each isotopologue and calibration of this quantity and calculation of isotope ratio has been thoroughly examined for CO<sub>2</sub> isotopologue spectrometers<sup>18, 21</sup>. Here we apply the same principles to calibrate our CH<sub>4</sub> isotopologue spectrometer. The uncalibrated instrument response varies linearly with the amount fraction for each isotopologue independently:

$$I_{211} = a_{211} Y_{211} + b_{211} \quad (3)$$

$$I_{311} = a_{311} Y_{311} + b_{311} \quad (4)$$

$$I_{212} = a_{212} Y_{212} + b_{212} \quad (5)$$

The calibration values gradient ( $a_i$ ) and intercept ( $b_i$ ) are determined for each isotopologue using the pair of AF PRMs, CS-L and CS-H (listed in Table 1), and are recalculated for each cycle of the instrument. The isotopologue amount fractions  $Y_{211}$ ,  $Y_{311}$  and  $Y_{212}$  for the calibration standards are determined from the gravimetric amount fraction and the assigned  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ , using the method described in the supporting information S3. Each AF PRM is analysed within a preconcentrator cycle, followed by the preconcentrator sample. The calibration parameters show drift between runs, which we account for by linearly interpolating values for  $a_i$  and  $b_i$  over time. The calibration standards, CS-L and CS-H, bracket the samples (after preconcentration) in total  $\text{CH}_4$  amount fraction and are produced from the same pure  $\text{CH}_4$  source (Figure 4). The assignment of  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  to these calibration gases is described in supporting information S4.

We also perform a calibration method analogous to that used in IRMS (supporting information S3), and which is sometimes applied to optical measurements, to highlight any resulting differences in these approaches. Here, the ratio of uncalibrated instrument response is recorded for the sample and this ratio measured for the sample is calibrated using the same ratio measured for a standard. In a second step a phenomenological correction is applied for an amount fraction dependence.

## Results and Discussion

### Calibration and target sample analysis

We have characterised the performance of Boreas for measurements of each isotope ratio using the high AF PRMs (CT and ST) in  $\text{N}_2$  to verify the calibration accuracy and measurement repeatability of the Aerodyne spectrometer directly, and the whole-air standards (BT and H-354) to characterise the combined preconcentrator and spectrometer.  $\delta^{13}\text{C}$  has been measured for the AF PRM parent  $\text{CH}_4$  and whole-air standard, so a direct comparison is made.  $\delta^2\text{H}$  has not been measured by IRMS for any of the gases here, so only stability with respect to drift has been characterised.

#### $\delta^{13}\text{C}$ analysis

##### *Spectrometer characterisation*

The ratio and isotopologue calibration methods for Boreas show negligible differences in the calibrated values and precision for measurements of  $\delta^{13}\text{C}$  (Table 2). The assumption of linearity in the calibration approach was tested using the CT tank at  $550 \mu\text{mol mol}^{-1}$   $\text{CH}_4$  amount fraction, within the range of the two calibration AF PRMs, CS-L and CS-H ( $500 \mu\text{mol mol}^{-1}$  and  $626 \mu\text{mol mol}^{-1}$ ), all prepared from the same parent  $\text{CH}_4$  A462. Multiple analyses ( $n=116$ ) over the period of 1 week measured a difference of  $0.04 \text{‰} \pm 0.05 \text{‰}$  (1SD) from the expected value.

We apply the same calibration procedure for analysis of the spectrometer target AF PRM (ST), made from parent  $\text{CH}_4$  25977. Measurements made by IRMS show a difference of  $10.23 \text{‰} \pm 0.07 \text{‰}$  (1SD) between ST-d and CS-d (see Figure 4 for relationship between

parent CH<sub>4</sub>, high AF PRMs and near-ambient amount fraction samples). Our measurements using the spectrometer found a difference of  $10.07\text{‰} \pm 0.08\text{‰}$  for the ratio calibration method and  $10.09\text{‰} \pm 0.08\text{‰}$  for the isotopologue calibration method. The magnitude of difference between IRMS and the spectrometer is very small given the repeatability, shown as one standard deviation of many measurements. There are numerous other factors that could introduce a systematic difference between the measurements made by IRMS and Boreas' spectrometer, which are not accounted for when using repeatability as a simple measure of standard uncertainty. The assumed linearity over the range of amount fractions is validated by measurement of CT, and a full uncertainty budget analysis is beyond the scope of this study, however we explain some of the possible reasons. A major factor is the procedure for calibration; Boreas's spectrometer is directly measuring the difference between ST and CT, however the IRMS measurements are made relative to a working standard that is changed on a near-annual basis after around 2500 analyses. Small errors in any steps could propagate into a difference of this magnitude. Other contributing factors to the difference could include fractionation or contamination during preparations of the dilutions from both A462 and 25977 (Figure 4). Also, differences due to the measurement of bulk isotope ratios (IRMS) vs. a specific isotopologue ratio (laser spectroscopy) due to non-stochastic polyisotopic distributions could be a contributing factor. In this analysis of the ST we show that Boreas' laser spectrometer makes a robust measurement of isotopically distinct CH<sub>4</sub> by using AF PRMs of CH<sub>4</sub> of only a single isotopic composition for calibration. The difference we observe between samples with such a distinct isotopic composition (relative to our IRMS analysis) agrees favourably with the magnitude of differences seen across IRMS laboratories that employ more comparable and mature practices in measurement<sup>7</sup>.

#### *Preconcentrator characterisation*

To make a similar performance characterisation for ambient air samples (processed through the Boreas sampling and preconcentration system) we used analysis of BT and H-354. Measurement of BT and H-354 on Boreas showed an identical carbon isotopic composition (difference of  $0.00\text{‰} \pm 0.10\text{‰}$ , 1SD). Analysis of H-354 by IRMS measured lighter by  $0.26\text{‰} \pm 0.07\text{‰}$  (1SD) compared to Boreas – a small but significant difference. The reasons for such differences have been studied by the isotopic measurement community and such variations have often been attributed to the referencing strategy used, with the strategy of 'identical treatment' for sample and reference now being largely employed<sup>22</sup>.

Boreas attempts to process the air sample in a way as to create a pure CH<sub>4</sub> sample in N<sub>2</sub> to matrix-match with the spectrometer calibration AF PRMs (CS-L and CS-H). If we assumed the analysis by IRMS is more accurate than Boreas, then it is likely that the Boreas sample is therefore not sufficiently matrix matched. There is evidence for this in our analysis as the repeatability of BT is not as good as ST (AF PRM with pure CH<sub>4</sub> in N<sub>2</sub>) indicating that there is very slight variability in a matrix component that is not being accounted for in calibration. This has also been found to be the case in other studies utilising preconcentration methods. Eyer et al.<sup>12</sup> found a 2.3 ‰ offset in their analyses using a similar approach of preconcentration coupled to a laser spectrometer that they attributed to an increase in O<sub>2</sub> in their sample matrix to 40 % relative to the standards containing 20 %. They also show a decrease in performance between the laser spectrometer (0.1 ‰ precision estimated from Allan Variance) and the complete system (0.19 ‰ repeatability), which they attribute a variable O<sub>2</sub> content arising from trap temperature control stability. While we have not

quantified the matrix effect on Boreas measurements, the 10 mmol mol<sup>-1</sup> O<sub>2</sub> carry-over determined by GC in Section 0 would produce a 0.12 ‰ offset relative to our O<sub>2</sub>-free standards, assuming the same proportionality.

If and how to correct for any offset observed between laboratories is a topic of significant interest in isotope ratio metrology<sup>7</sup>, with much research taking place on how to create both common reference materials and protocols for measurement and analysis. Understanding the origin of remaining inaccuracies in analysis<sup>7, 23</sup> is also a topic of interest. To accelerate the combined use of different measurement datasets, a pragmatic approach is often taken. The offset between laboratories is monitored by inter-comparison studies and applied as a correction, which allows the modelling community to utilise the measurements appropriately and without causing biases in the model output. To this end, we measure the BT between every air sample. This allows us to both monitor the stability of the instrument and apply an appropriate, continuously-measured offset to the air data to ensure compatibility with at least one IRMS measurement dataset (in our case that of Royal Holloway, University of London, see Supporting Information). The typical repeatability on the four measurements of BT spanning a single air measurement is 0.048 ‰, and thus, applying an offset to each air measurement we calculate an estimated propagated standard uncertainty on a single air measurement of 0.07‰.

One potential inaccuracy in applying an offset correction is its dependence on amount fraction in the spectrometer. This would, however, have a negligible influence owing to the fact that we only see a very small amount fraction dependence in the coefficients of the calibration equations (Section S3) and that the majority of the calibration is achieved with the synthetic standards.

**Table 2** The isotopic ratio and associated repeatabilities of the target sample measurements

Target tank	Calibration method	$\delta^{13}\text{C}$ (‰)			$\delta^2\text{H}$ (‰)		
		Mean	Repeatability (1SD) <sup>#</sup>	Average rolling repeatability (1SD) <sup>§</sup>	Mean	Repeatability (1SD) <sup>#</sup>	Average rolling repeatability (1SD) <sup>§</sup>
<b>Calibration target</b>	<i>Ratio</i>	-51.54	0.055	0.033	-192.79	0.22	0.17
	<i>Isotopologue</i>	-51.54	0.055	0.033	-192.66	0.29	0.27
<b>Spectrometer target</b>	<i>Ratio</i>	-41.47	0.057	0.038	-191.05	0.28	0.20
	<i>Isotopologue</i>	-41.45	0.057	0.038	-190.46	0.29	0.27
<b>Boreas target</b>	<i>Ratio</i>	-47.15	0.079	0.055	-90.48	1.18	0.61
	<i>Isotopologue</i>	-47.14	0.083	0.048	-92.63	1.32	0.74

<sup>#</sup> Repeatability of measurements over seven days from 17th -23rd December 2020. Number of measurements were 116, 116 and 58 for calibration target, spectrometer target and Boreas target, respectively.

<sup>§</sup> A repeatability of 4 sequential measurements was calculated and these were averaged across the same six days

### $\delta^2\text{H}$ analysis

There is again evidence of a small, variable matrix effect in the repeatability of the different target samples (CT, ST and BT). The repeatability of ST over a week of measurements (0.29‰, 1SD, n=116) was similar to the average of the 4-point repeatability over the same time period (0.27‰). For BT, however, long-term repeatability was almost double that of the average 4-point repeatability at 1.32‰ and 0.74‰, respectively.

We also found a small but significant difference in the calibrated  $\delta^2\text{H}$  using the ratio or isotopologue methods. We attribute this to the greater amount fraction-dependency for the measurement of  $\delta^2\text{H}$  compared with  $\delta^{13}\text{C}$ . <sup>12</sup>CH<sub>3</sub>D is measured using the second laser in the spectrometer, as the absorption signal from this isotopologue is much smaller than the more

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3 dominant molecules, so is measured in a different region of the spectrum. Also, the strong  
4  $^{12}\text{CH}_4$  absorption recorded by laser 1 is still used to calculate the ratio  $r$ . Consequently, this  
5 ratio has a different response in proportion to amount fraction. The intercept term in the  
6 spectrometer calibration (3) for  $^{12}\text{CH}_4$  is about  $b_{211} = 5 \mu\text{mol mol}^{-1}$ , which is  $\sim 1\%$  of the  
7 magnitude under the nominal composition used here; for  $^{12}\text{CH}_3\text{D}$  this is  $b_{212} = 15$   
8  $\mu\text{mol mol}^{-1}$ , or  $\sim 4\%$ . This has the effect of increasing the apparent amount fraction  
9 dependence of the instrument response ratio  $I_{212}/I_{211}$  and limits the accuracy of the  
10 phenomenological correction. This correction factor for the deuterated isotopologue is  $m$   
11  $(\delta \text{D}) = 0.0376\text{‰} / \mu\text{mol mol}^{-1}$  compared with  $m(\delta^{13}\text{C}) = -0.00161 \text{‰} / \mu\text{mol mol}^{-1}$ .  
12 As shown by Griffith<sup>17</sup> calibration of the  $\delta$  value obtained directly from the spectrometer  
13 response requires a correction term inversely proportional to amount fraction, so the scaling  
14 factor used here is an approximation that is sufficient for only small corrections. The  
15 comparison for the calibration target given in Table 2 indicates that this is the case for  $\delta^{13}\text{C}$   
16 but not for  $\delta^2\text{H}$  in this instrument, where the isotopologue method produces more accurate  
17 results with a smaller difference to the expected values of  $\delta^{13}\text{C} = -51.50 \text{‰}$  and  $\delta\text{D}$   
18  $= -192.70 \text{‰}$ . Note that the overall precision expressed as the repeatability is similar for  
19 both, showing that both the isotopologue and ratio calibration methods perform equally with  
20 instrumental noise and drift in this laser spectrometer.

### 27 **Ambient air measurement time series**

28 Air is continuously drawn into a laboratory at NPL from a sampling inlet on the roof (17  
29 metres above ground level, 51.424149° N, 0.343872° W). Boreas samples from this  
30 continuous flow, which minimises dead volume in the sampling lines and reduces the amount  
31 of flushing time needed before Boreas begins sampling. Our analysis period spans mid-  
32 December 2020 to mid-February 2021. During this time there are two breaks in the  
33 measurements. On 24<sup>th</sup> December the repeatability began to deteriorate as was seen in both  
34 the ST measurements (sample loaded straight into spectrometer) and in the BT  
35 measurements, indicating an issue with the spectrometer rather than the sampling and  
36 preconcentration. The spectrometer laser path was re-adjusted and characteristic performance  
37 of the instrument resumed. This is a highly unusual intervention that should only be required  
38 very rarely. Shortly after this, however, a hardware fault in the sampling system took the  
39 instrument offline until mid-January. Once characteristic performance resumed the  
40 instrument was taken offline for two weeks for further tests of the system and analyses (e.g.  
41 measurement of H-354 for inter-comparison with IRMS). Following this the instrument  
42 began continuous measurements from 1<sup>st</sup> February. During this period there have been no  
43 necessary changes of carrier gas, calibration, or target gases. A 40 l (water volume), 200 bar  
44 cylinder of  $\text{N}_2$  lasts over three months, a 50 l volume 200 bar BT cylinder lasts  $>6$  months  
45 (assuming 10 measurements a day), and the 10 l volume 100 bar synthetic AF PRMs last  $>12$   
46 months. Assuming normal operation without faults Boreas could therefore operate  
47 continuously with an optimum calibration strategy for  $>6$  months (assuming automated  
48 changeover exists for the  $\text{N}_2$  carrier gas or if a  $\text{N}_2$  generator was employed). Figure 5 shows  
49 the results for  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  measurements from this recent period of ambient air analysis.  
50 Accurate ambient air amount fraction measurements are critical for quantitative interpretation  
51 of the isotope ratios and our approach with Boreas is explained in the supporting information  
52 S5. The measurements of BT are also shown to illustrate the repeatability of Boreas relative  
53 to the magnitude of changes in ambient air. The standard uncertainty of  $\delta^2\text{H}$ , estimated from  
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the rolling standard deviation of 4 measurements, relative to the magnitude of changes seen in the atmospheric samples is particularly small as compared with the same dataset for  $\delta^{13}\text{C}$ . Simultaneous analysis of both isotopes systems using a single instrument will prove highly valuable for interpretation of atmospheric  $\text{CH}_4$  (e.g. as illustrated by Menoud et al.<sup>11</sup> for identifying fossil source  $\text{CH}_4$  in Krakow, Poland). The most significant pollution event (occurring at the end of 2020) shows a particularly heavy  $\delta^{13}\text{C}$  signature, yet a light  $\delta^2\text{H}$  signature is maintained, indicating the significant potential for these measurements for emissions source apportionment.

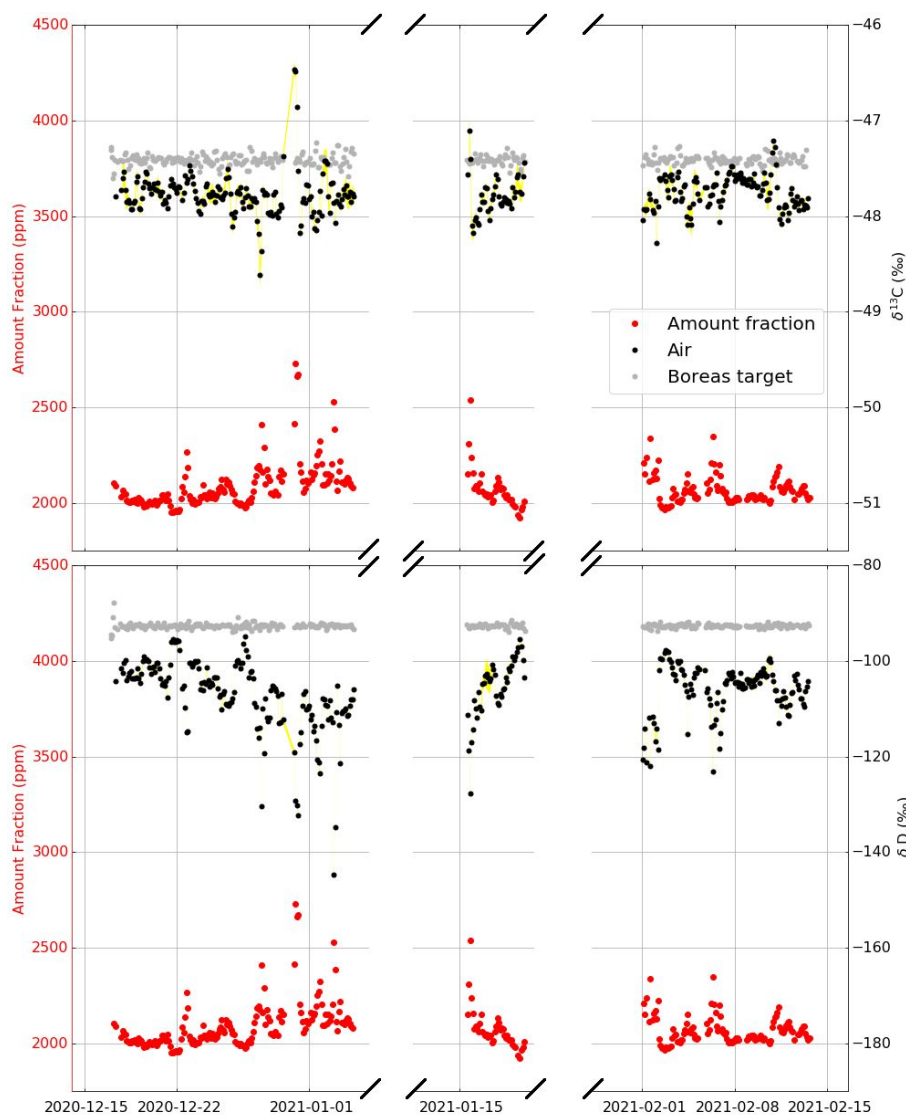


Figure 5 Boreas ambient air time series of  $\delta^{13}\text{C}$  (top) and  $\delta^2\text{H}$  (bottom) measurements made at NPL from a roof sampling inlet. The same offset is applied to both the BT and air measurements – in this example enabling the  $\delta^{13}\text{C}$  dataset to be directly comparable to measurements by RHUL. For  $\delta^2\text{H}$  we have applied an equivalent correction based on an assigned value for BT of  $-92.63\text{‰}$ .

## Conclusions

We have developed an instrument able to monitor both  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  simultaneously in ambient air. We have devised a continuous instrument calibration procedure that is able to estimate the standard uncertainty of each ambient air measurement, based on the measurements of a suite of synthetic AF PRMs and compressed whole-air working standards.

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3 The system is fully automated, able to make a single air measurement at least every 150  
4 minutes (based on every sample bracketed by a compressed whole air standard), which is of a  
5 frequency that allows for coupling to high temporal and spatial resolution atmospheric  
6 transport models. The additional information provided through isotopic analyses could help  
7 quantitatively estimate sectoral emissions of CH<sub>4</sub> on country to regional scales, providing a  
8 tool for policy makers looking to make the most efficient gains in emission reductions over  
9 the coming years. Analytically there is potential for the instrument to improve further in  
10 precision and accuracy of measurement and to rival IRMS measurement as a high  
11 specification instrument able to continuously measure more than one isotope system  
12 simultaneously and with low maintenance cost. The performance for δ<sup>2</sup>H is particularly  
13 favourable relative to IRMS analysis and opens up the possibility for in situ high precision  
14 global measurements of δ<sup>2</sup>H at remote monitoring observatories.  
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## Supporting Information

The following Supporting Information is available free of charge at the [ACS website](#): S1 The CH<sub>4</sub> 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<sub>4</sub> amount fraction in ambient air

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