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

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Abstract

We present a new instrument, 'Boreas', a cryogen-free methane (CH_4) preconcentration system coupled to a dual laser spectrometer for making measurements of δ^{13}C(CH_4) and δ^2H(CH_4) (simultaneously) in ambient air. Excluding isotope ratio scale uncertainty, we estimate typical standard measurement for an ambient air sample of 0.07 ‰ for δ^{13}C(CH_4) and 0.9 ‰ for δ^2H(CH_4), which is the lowest reported for a laser spectroscopy-based system and comparable to isotope ratio mass spectrometry. We trap CH_4 (~1.9 µmol mol^{-1}) from ~5 l of air onto the front end of a packed column, subsequently separating CH_4 from interferences using a controlled temperature ramp with N_2 as the carrier gas, before eluting CH_4 at ~550 µmol mol^{-1}. This processed sample is then delivered to an infrared laser spectrometer for measuring the amount fractions of $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ isotopologues. We calibrate the instrument using a set of gravimetrically prepared primary reference materials (PRMs) directly into the laser spectrometer that span a range of 500 µmol mol^{-1} to 626 µmol mol^{-1} (CH_4 in N_2) made from a single pure CH_4 source that has been isotopically characterised for δ^{13}C(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 δ^{13}C(CH_4) and δ^2H(CH_4) in over 200 ambient air samples and demonstrate the application of Boreas for deployment to atmospheric monitoring sites.

1. Introduction

Methane (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

that of carbon dioxide (CO_2)[1]. Mitigation of CH_4 emissions therefore plays a vital role in tackling the climate crisis. Unlike CO_2 that has shown a very consistent rise in the atmosphere over the last century, owing to anthropogenic fossil fuel emissions, CH_4 has gone through periods of small changes in the growth rate for reasons that are poorly understood[2]. CH_4 is emitted from a variety of sources and processes, and largely removed by chemical destruction in the troposphere (global atmospheric lifetime of ~decade[2]). Although anthropogenic emissions have been a clear main driver of the rising global atmospheric concentrations over the last century, the sectoral (e.g. agricultural versus energy), temporal and spatial disaggregation of emissions remains poorly quantified and difficult to verify through atmospheric measurements of amount fractions alone[3]. While the main thrust of the widespread mitigation measures needed is very clear (eliminate fugitive leaks during fossil fuel extraction and transport and develop low-emission agricultural methods) the measurement tools to aid timely, efficient and equitable policy decision making are lacking[3].

Different formation, transport, and removal processes can impart distinctive isotopic fractionations on molecules[4]. These naturally-occurring isotopic labels provide an extra layer of information for studying biogeochemical cycling and anthropogenic emissions[3, 5]. Isotopic composition, typically measured by isotope ratio mass spectrometry (IRMS), has provided key insights into our understanding of the historical and contemporary global atmospheric budgets[5]. Isotopic records are largely constructed by continuous or one-off sampling campaigns followed by analysis in the laboratory by isotope ratio mass spectrometry[6]. The high-quality measurements needed for such studies are difficult to make, time consuming and expensive, and only performed by fewer than 20 laboratories across the world[7]. In populated regions such as Europe different types of emission sources are in proximity, making it difficult to usefully verify emissions (i.e. quantitatively separate different sources) using atmospheric measurements. However, in bringing together the source-specific information gained from isotopic observables and the benefits of coupling high-frequency measurements with high-resolution atmospheric chemistry transport model (ACTM) output, we will be able to make a significant improvement in our quantitative understanding of sector-specific fluxes[8-9]. To this end, impressive attempts have been made to take IRMS systems to atmospheric observatories for high precision, in situ, frequent analysis of both $\delta^{13}C(CH_4)$ and $\delta^2H(CH_4)$ [9-10]. These studies generated thousands of measurements over many months providing data that could be assimilated into ACTMs for interpretation.

Instruments such as Fourier transform infrared or laser absorption spectrometers, can make high-frequency measurements with low maintenance requirements. However, commercial spectrometers are unable to make sufficiently high-precision $\delta^{13}C(CH_4)$ and $\delta^2H(CH_4)$ measurements due to the low abundance of CH_4 in ambient air, which results in a poor signal-to-noise ratio (currently dry air amount fractions in the well-mixed atmosphere are <2 μmol mol^{-1}). One method to improve the signal-to-noise ratio is to concentrate the analyte of interest out of ambient air for analysis with a commercially-available spectrometer. Eyer et al.[11] made progress in developing this approach for simultaneous measurements of $\delta^{13}C(CH_4)$ and $\delta^2H(CH_4)$ by laser spectroscopy, and later showed the potential for these more efficient measurement systems to be deployed[9]. The measurement repeatability (0.19‰ for $\delta^{13}C$ and 1.9‰ for δ^2H), however, was significantly larger than those of laboratory-based IRMS methods (<0.05‰ for $\delta^{13}C$ and 1‰ for δ^2H). 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 O_2 content of the trapped sample that goes 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 CH_4 using synthetic gravimetrically-prepared standards.

2. Methods

2.1 Overview

The limitations to using infrared laser absorption spectroscopy for isotope ratio measurement of atmospheric methane arise from the weak signals due to low ambient amount fraction and interference from other gases. There is minimal direct interference from overlapping features in the spectral region used here, but there is significant indirect interference where different matrix gases cause changes in the pressure broadening of the line profiles that results in bias in the amount fraction calculated from a spectral fit. It is necessary to normalise the matrix of the sample with respect to the spectrometer calibration standards which is achieved in Boreas by separating methane from the other constituents on a cold trap then transferring this to the spectrometer using pure nitrogen.

Boreas is constructed from three distinct connected parts: 1) a purpose-built unit for sampling, CH_4 preconcentration, and matrix normalisation; 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 PRMs of CH_4 in N_2. Whole-air target gas working standards are treated the same as an air sample to monitor performance. The system is fully automated and alarmed allowing continuous remote operation for weeks with high purity N_2 carrier gas and standard gases as the only consumables.

2.2 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 cm^{-1} to 1293.816 cm^{-1} for $^{12}CH_4$ and $^{13}CH_4$ and 1306.883 cm^{-1} to 1307.077 cm^{-1} for $^{12}CH_4$ and $^{12}CH_3D$. The resulting spectrum is fitted for the amount fraction of the isotopologues using parameters from the Hitran2016 database[12], and a polynomial baseline. Details are given in the supporting information S1.

Sampling and matrix normalisation

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 K with minimal heat load, and at 100 K has a lift of >20 W. The cold end of this cryo-cooler is housed in a vacuum for thermal isolation (below 10^{-6} mbar pumped by an Edwards

nEXT85D turbomolecular pumping station), interfaced with the sample gas via a trap tube (stainless steel, 1.5 m long, 1/8" outside diameter, 2.0 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^3, which is comparable to other systems such as the Medusa GC-MS and TREX which have trapping volumes of 1544 mm^3 and 6363 mm^3, respectively[11, 13]. 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[13-15], 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$_2$ 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).
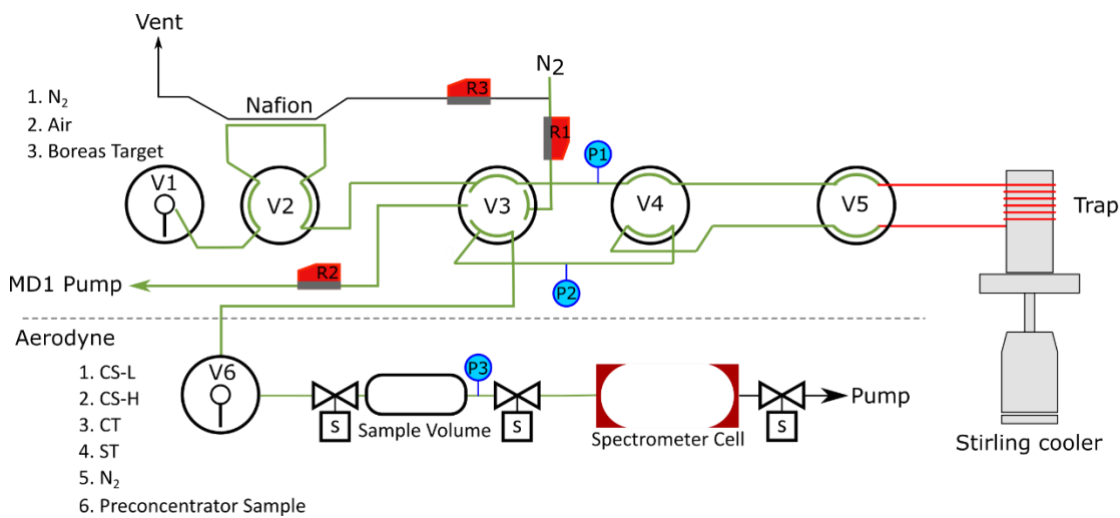

Figure 1 Flow scheme for the sampling of methane from ambient air and delivery to the laser spectrometer. Valves 1-6 (V1-V6), mass flow controllers (R1-R3) and the pressure transducers (P1-P3) are labelled. The solenoid valves are denoted by the squared "S". The sampling volume and spectrometer cell are notated in the figure. Multi-selector V1 has 3 ports connected; (1) N2; (2) air; and (3) the Boreas Target from Mace Head. Multi-selector V6 has 6 ports connected that lead to the spectrometer; (1) low calibration standard PRM (CS-L); (2) high calibration standard PRM (CS-H); (3) calibration target PRM (CT); (4) spectrometer target PRM (ST); (5) pure N2; 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 of trapping, methane separation, methane elution and trap reconditioning before the trap is allowed to cool for the next cycle.

(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 ~580 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 N_2 (Air Products, BIP purity) counter-purge at a flow rate of 200 ml min^{-1} during sampling and 20 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 region (a) in

Figure 2. The sample flows through the trap starting at ~113 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 K). Trace gases from around ~5 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 during 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 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 ml min^{-1} and then 10 ml min^{-1} with 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 ~360 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 methane into the sampling volume, using the procedure described below.

(d) Reconditioning 1620 s to 1950 s)

At the end of the methane 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_2O). The heating is then cut off and the trap allowed to cool passively via the dissipation of heat through the cryocooler.
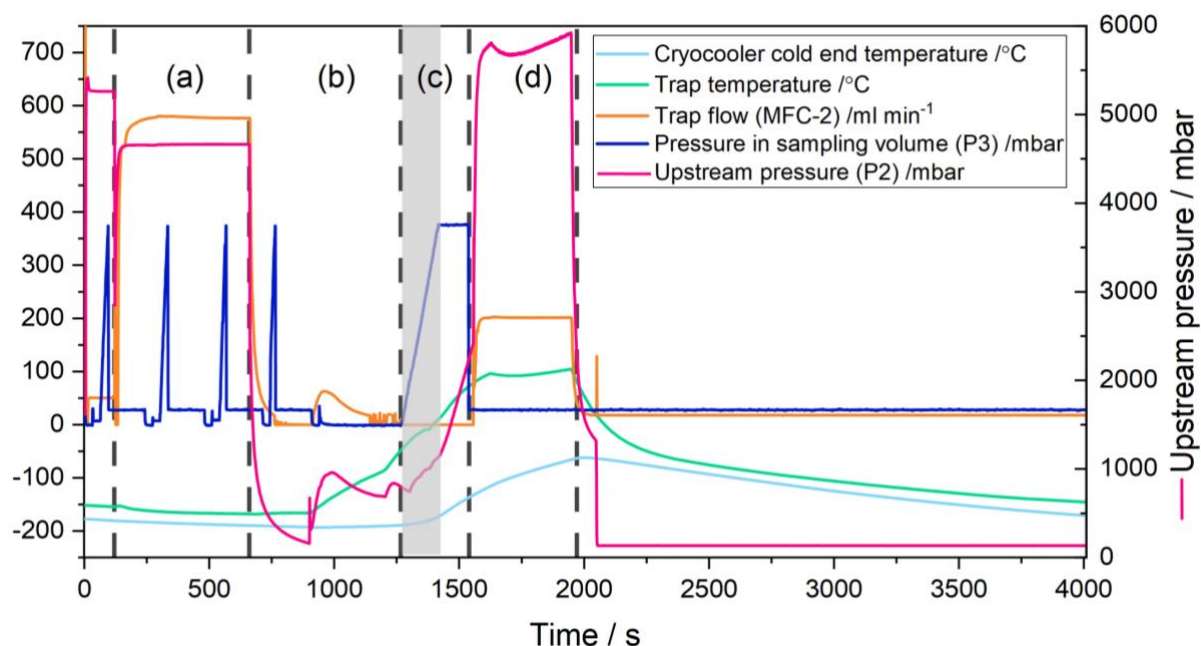

Figure 2 Stripchart of various instrument parameters during a run. Top (left axis): Cryocooler cold end temperature; trap temperature (thermocouple attached midway on outside of the trap tubing); trap flow (recorded by the mass-flow controller down-stream of the trap); sampling volume pressure (Figure 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) methane separation (c) methane elution (d) reconditioning. The bottom plot shows the CH_4 and N_2O elution profile during trap heating, calculating by systematically changing the time in the run at which the sampling volume is opened to the trap (each data point represents a result from a separate run cycle). The grey box highlights the optimised period that the trap is open to the sampling volume.

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_4 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) of 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 a PRM or the trap is loaded into the spectrometer and analysed, automated by the spectrometer software. The trap eluent contains varying amounts and possibly different isotopic compositions of CH_4 (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 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.

3. Measurement protocols and calibration methodology

3.1 Laser spectrometer measurement acquisition

Once in the laser spectrometer cell the sample 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. 100 seconds of reported amount fraction data 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.

3.2 Optimisation of CH_4 elution from the trap

Quantitative capture of CH_4 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_2O). To this end, we use the HaysepD trap also as a chromatographic column by fore-flushing CH_4. This allows volatile gases such as O_2 to be largely removed before elution of CH_4, while variable and less volatile gases such as N_2O 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. The sample volume fills to the same 375 mbar pressure in each of these runs with the flushing N_2 and the measured methane amount fraction shows a clear maximum around the optimum time delay. The methane amount fraction as a function of time delay effectively shows the time profile for methane 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 methane amount fraction from two consecutive runs and dividing this by the difference by the difference in transfer time delay between the runs (10 s). Figure 3 plots this estimate for the CH_4 and N_2O spectrometer signals for a set of different transfer time delays, which shows that the chosen transfer delay time and duration, represented by the gray shading, completely encloses the CH_4 peak and significant separation (~90 s) between the end of CH_4 elution and the start of N_2O, allowing the sampling volume to be closed off before N_2O elution.
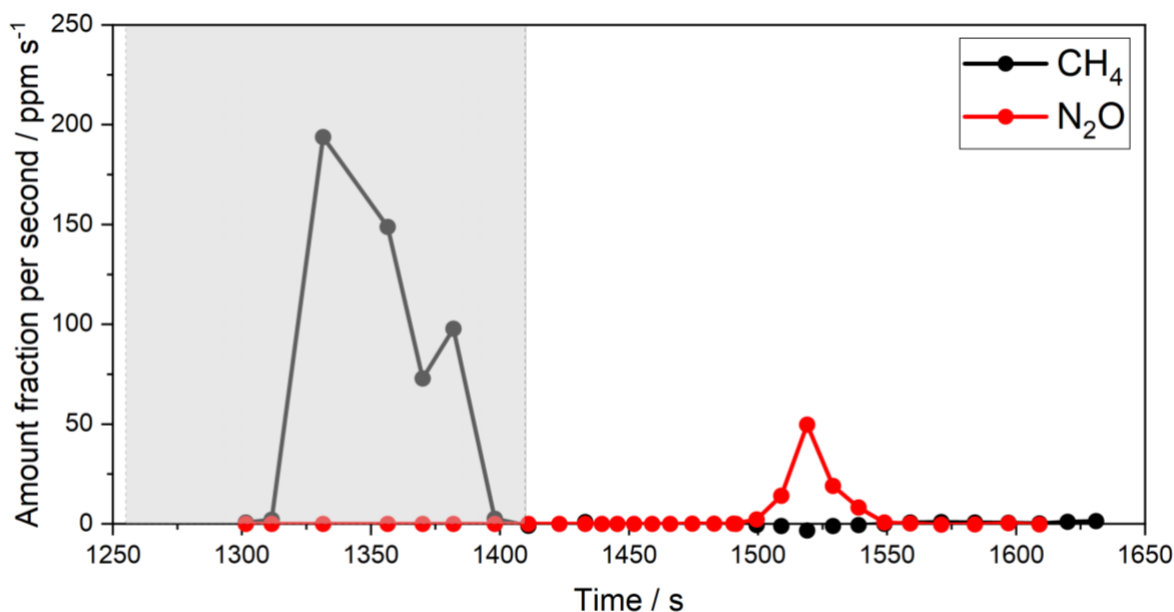
Figure 3 Elution profile of CH$_4$ and N$_2$O from the trap, reconstructed by a deconvolution procedure described in the text. Each point is a separate instrument cycle and the spectrometer measures CH$_4$ and N$_2$O simultaneously for each sample. The time axis is the relative to the start of the cycle and the shaded region indicates the valve timing selected as the optimum during which the sample volume is filled. This matches the shading in

Figure 2.

We analysed the composition of the Boreas trap eluent (collected under optimised conditions) for other major gases that were concentrated and elute together with CH$_4$ 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^{-1} CH$_4$ in the pure N$_2$ carrier gas plus trace amounts of other air components more volatile than methane such as oxygen, argon and krypton. This eluant was transferred to an evacuated 10 l (water volume) gas cylinder and diluted in He (Air Products, BIP) to pressurise the mixture for analysis by gas chromatography. The dilution factor from helium addition is estimated as 0.02% from the accurate mass of each addition determined by gravimetry and assuming the eluant is pure N$_2$ 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 helium ionisation detector (PDHID). By comparison with NPL in house standards, the amount fraction of oxygen in the sample was calculated as (10 ± 1) mmol mol^{-1}. The concentrations of other permanent gases (Kr and Ar) in the sample were < 0.5 mmol mol^{-1}.

3.3 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$_4$ necessarily leads to alteration of the ambient air

matrix i.e. the proportion of O_2 to N_2 and noble gases. We therefore aimed to concentrate CH_4 from air on the trap and then remove the CH_4 from the trap with pure N_2 carrier gas (as described in Section 2.2).

This approach has significant potential for developing a long term, simplified and traceable calibration strategy: If the CH_4 from air can be transferred to a pure-N_2 matrix (i.e. the preconcentrator both boosts the sensitivity of the spectrometer and normalises the matrix) then synthetic 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, an accurate isotope ratio measurement can be made[16-17].

Calibration standards and targets

Two high amount fraction PRMs prepared from methane in nitrogen 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 amount fraction PRMs are used to validate the spectrometer calibration: one named calibration target containing methane from the same source as CS-L and CS-H, and one named spectrometer target containing methane from a different parent batch (CT and ST). Two compressed whole air samples (BT, H-354) were used to calibrate and characterise Boreas's performance by sampling through the preconcentrator. Two other PRMs for analysis by mass spectrometry were prepared, with a methane amount fraction near ambient, by diluting the CT and ST by further addition of nitrogen.
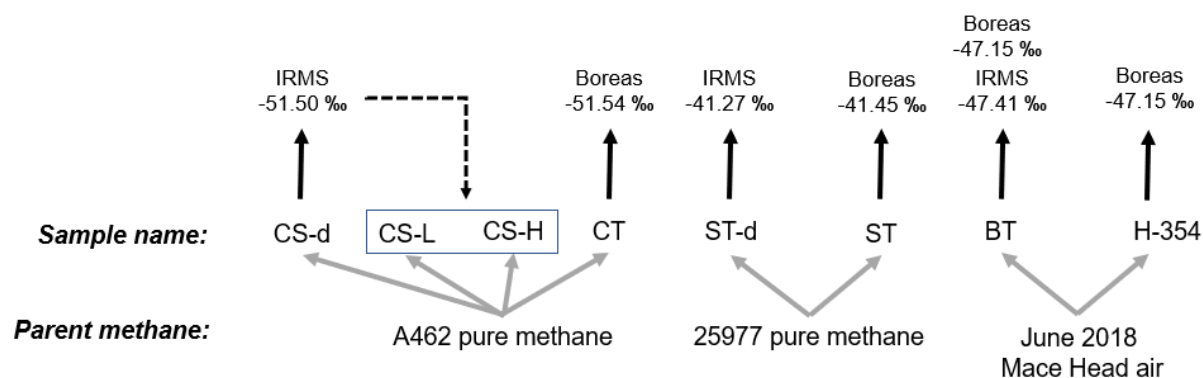

Figure 4 Schematic of the relationship between parent CH4, PRMs, whole air standards, and measurements made for $\delta^{13}C$. Grey arrows represent physical dilution of the parent CH4 for preparation of the PRMs. All Boreas measurements shown here are made using calibration of the spectrometer using two synthetic mixtures CS-L and CS-H with 500 µmol mol^{-1} and 626 µmol mol^{-1} amount fractions in nitrogen, 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_4 source and the mixtures prepared for measurement by Boreas and IRMS. The PRM calibration standards (CS-L, CS-H) and calibration target (CT) were prepared gravimetrically by diluting a 2.23% CH_4 (N6.0, CK gases) parent standard to 500 µmol mol^{-1}, 626 µmol mol^{-1} and 550 µmol mol^{-1}, using high-purity N_2 (N6.8 grade BIP+, Air Products). The CH_4 for ST came from another source (25977 technical grade 2.5, Air Products) diluted to 600 µmol mol^{-1} using the same high-purity N_2. These synthetic 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 ~200 bar [18]. 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 (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 methane parents. The samples listed below the dashed line were all measured for $\delta^{13}C$ by IRMS and these values assigned to mixtures prepared from the same parent. Values without an uncertainty represent assigned $\delta^{13}C$ based on measurements by IRMS, or for δ^2H based on the scale anchor point from BT as described in supporting information S4.

Where an uncertainty is provided it indicates a $\delta^{13}C$ 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 CH and CL are not measured by Boreas but used as the 'known' calibration standards with assigned isotope ratios

n/m = not measured

Sample name (NPL ID)	CH$_4$ origin (NPL ID)	Description	CH$_4$ (µmol mol^{-1})	NPL Boreas		Externally measured or assigned values		
				$\delta^{13}C$ (1SD, n) (‰)	δ^2H (1SD, n) (‰)	$\delta^{13}C$ (1SD, n) (‰)	δ^2H (1SD) (‰)	$\delta^{13}C$ Boreas offset (‰)
CS-L (NPL-2635)	CK gases (A462)	Low calibration standard PRM	500.1	n/a	n/a	-51.50	-192.70	n/a
CT (NPL-A662)	CK gases (A462)	Calibration target 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 PRM	625.5	n/a	n/a	-51.50	-192.70	n/a
ST (NPL-2833)	Air Products (25977)	Spectrometer target 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 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 PRM for IRMS analysis	2.006	n/m	n/m	**-51.50 (0.04, 12)**	**-192.70**	**Zero (anchor point)**
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

A sample of each pure methane parent, diluted to near-ambient amount fraction in nitrogen (CS-d and ST-d), and the whole-air standard BT were analysed at Royal Holloway University of London (RHUL) for $\delta^{13}C$, as described in the supporting information S4. $\delta^{13}C$ has been assigned for the calibration standards by IRMS measurement, however δ^2H has not been directly measured. We estimate an assignment for δ^2H 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

$$\delta^{13}C = \frac{Y_{311}/Y_{211}}{R_{VPDB}} - 1 \tag{1}$$

$$\delta^2H = \frac{Y_{212}/Y_{211}}{R_{VSMOW}} - 1 \tag{2}$$

where $Y_{211} \equiv Y(^{12}CH_4)$, $Y_{311} \equiv Y(^{13}CH_4)$ and $Y_{212} \equiv Y(^{12}CH_3D)$ are the calibrated amount fractions of $^{13}CH_4$, $^{12}CH_4$ and $^{12}CH_3D$, respectively (following the notation in Griffith[16] 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). 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_4. Recently there has been significant developments in 'clumped' isotopic CH_4 geochemistry and it is clear that any difference between bulk isotope ratios and isotopologue ratios is below the experimental uncertainty of our measurements[19]. For conciseness we keep the notation $\delta^{13}C$ to refer to $\delta^{13}C$ (CH_4), and δ^2H to refer to $\delta^2H(CH_4)$, when discussing results.

Calibration method
There are two approaches to calibrating an instrument response to produce a calibrated isotope ratio, for example $\delta^{13}C$ relative to the VPDB scale, that relates to the order of operations. The first method is to calibrate the measured isotopologue amount fraction of $^{13}CH_4$ and $^{12}CH_4$ 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 $^{13}CH_4$ to $^{12}CH_4$ (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 $^{13}CH_4$ and $^{12}CH_4$ 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_2 isotopologue spectrometers[17, 20]. Here we apply the same principles to calibrate our CH_4 isotopologue spectrometer. The uncalibrated instrument response varies linearly with the amount fraction for each isotopologue independently:

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

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

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

The calibration values gradient (a_i) and intercept (b_i) are determined for each isotopologue using the pair of amount fraction 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 $\delta^{13}C$ and $\delta^{2}H$, using the method described in the supporting information S3.1. Each amount fraction 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 CH4 amount fraction and are produced from the same pure CH4 source (Figure 4). The assignment of $\delta^{13}C$ and $\delta^{2}H$ to these calibration gases is described in supporting information S4.

We also perform a calibration method analogous to that used in IRMS (supporting information S3.2), 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 (e.g. $r = I_{311}/I_{211}$) 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.

4. Results and Discussion
4.1 Calibration and target sample analysis
We have characterised the performance of Boreas for measurements of each isotope ratio using the high amount fraction PRMs (CT and ST) in nitrogen 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. $\delta^{13}C$ has been measured for the PRM parent methane and whole-air standard, so a direct comparison is made. δD has not been measured by IRMS for any of the gases here, so only stability with respect to drift has been characterised.

$\delta^{13}C$ analysis

Spectrometer characterisation
The ratio and isotopologue calibration methods for Boreas show negligible differences in the calibrated values and precision for measurements of $\delta^{13}C$ (Table 3). The assumption of linearity in the calibration approach was tested using the CT tank at 550 µmol mol^{-1} CH4 amount fraction, within the range of the two calibration PRMs, CS-L and CS-H (500 µmol mol^{-1} and 626 µmol mol^{-1}), all prepared from the same parent CH4 A462. Multiple analyses (n=116) over the period of 1 week measured a difference of 0.04 ‰ ± 0.05 ‰ (1SD) from the expected value.

We apply the same calibration procedure for analysis of the spectrometer target PRM (ST), made from parent CH4 25977. Measurements made by IRMS show a difference of 10.23 ‰ ± 0.07 ‰ (1SD) between ST-d and CS-d (see Figure 3 for relationship between parent CH4,

high amount fraction PRMs and near-ambient amount fraction samples). Our measurements using the spectrometer found a difference of 10.07 ‰ ± 0.08 ‰ for the ratio calibration method and 10.09 ‰ ± 0.08 ‰ 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_4 by using PRMs of CH_4 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 very favourably with the magnitude of differences seen across IRMS laboratories that employ more comparable and mature practices in measurement[7].

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‰ ± 0.10‰, 1SD). Analysis of BT by IRMS measured lighter by 0.26‰ ± 0.07‰ (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[21].

Boreas attempts to process the air sample in a way as to create a pure CH_4 sample in N_2 to matrix-match with the spectrometer calibration 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 (PRM with pure CH_4 in N_2) 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.[11] found a 2.3 ‰ offset in their analyses using a similar approach of preconcentration coupled to a laser spectrometer which they attributed to an increase in oxygen in their sample matrix to 40 % relative to the standards containing 20 %. While we have not quantified the matrix effect on Boreas measurements, the 10 mmol mol^{-1} oxygen carry-over determined by GC in Section 3.2 would produce a 0.12 ‰ offset relative to our oxygen-free standards, assuming the same proportionality.

There is a small degradation from the repeatability of the laser spectrometer measurement of a high amount fraction sample (0.055 ‰) to the repeatability of the complete instrument to an ambient sample (0.083 ‰), taken as the standard deviation of 4 consecutive runs. This difference is likely due to run to run variability in the matrix. The instrument described in in Eyer *et al* also shows 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 oxygen content arising from trap temperature control stability.

If and how to correct for any offset observed between laboratories is a topic of significant interest in isotope ratio metrology[7], 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[7, 22] is also a topic of interest. To accelerate the combined use of different measurement datasets a pragmatic approach is often taken whereby 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). 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 ~94% of the calibration is achieved with the synthetic standards and only ~6% using an offset correction based on a comparison with IRMS.

Table 3 The isotopic ratio and associated repeatabilities of the target sample measurements

Target tank	Calibration method	δ¹³C (‰)			δ²H (‰)		
		Mean	Repeatability (1SD)[#]	Average rolling repeatability (1SD)[$]	Mean	Repeatability (1SD)[#]	Average rolling repeatability (1SD)[$]
Calibration target	*Ratio*	-51.54	0.055	0.033	-192.79	0.22	0.17
	Isotopologue	-51.54	0.055	0.033	-192.66	0.29	0.27
Spectrometer target	*Ratio*	-41.47	0.057	0.038	-191.05	0.28	0.20
	Isotopologue	-41.45	0.057	0.038	-190.46	0.29	0.27
Boreas target	*Ratio*	-47.15	0.079	0.055	-90.48	1.18	0.61
	Isotopologue	-47.14	0.083	0.048	-92.63	1.32	0.74

[#] 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.
[$] A repeatability of 4 sequential measurements was calculated and these were averaged across the same six days

δ²H 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 δ^2H using the ratio or isotopologue methods. We attribute this to the greater amount fraction-dependency for the measurement of δ^2H compared with $\delta^{13}C$. $^{12}CH_3D$ is measured using the second laser in the spectrometer, as the absorption signal from this isotopologue is much smaller than the more dominant molecules, so is measured in a different region of the spectrum. Also, the strong $^{12}CH_4$ absorption recorded by laser 1 is still used to calculate the ratio r. Consequently, this ratio has a different response in proportion to amount fraction. The intercept term in the spectrometer calibration (3) for $^{12}CH_4$ is about $b_{211} = 5$ µmol mol^{-1}, which is ~1 % of the magnitude under the nominal composition used here; for $^{12}CH_3D$ this is $b_{212} = 15$ µmol mol^{-1}, or ~4 %. This has the effect of increasing the apparent amount fraction dependence of the instrument response ratio I_{212}/I_{211} and limits the accuracy of the phenomenological correction. This correction factor for the deuterated isotopologue is $m(\delta D) = 0.0376‰ /$µmol mol^{-1} compared with $m(\delta^{13}C) = -0.00161$ ‰ / µmol mol^{-1}. As shown by Griffith[16] calibration of the δ value obtained directly from the spectrometer response requires a correction term inversely proportional to amount fraction, so the scaling factor used here is an approximation that is sufficient for only small corrections. The comparison for the calibration target given in Table 3 indicates that this is the case for $\delta^{13}C$ but not for δ^2H in this instrument, where the isotopologue method produces more accurate results with a smaller difference to the expected values of $\delta^{13}C = -51.50$ ‰ and $\delta D = -192.70$ ‰. Note that the overall precision expressed as the repeatability is similar for both, showing that both the isotopologue and ratio calibration methods perform equally with instrumental noise and drift in this laser spectrometer.

4.2 Ambient air measurement time series

Air is continuously drawn into a laboratory at NPL from a sampling inlet on the roof (17 metres above ground level, 51.424149° N, 0.343872° W). Boreas samples from this continuous flow, which minimises dead volume in the sampling lines and reduces the amount of flushing time needed before Boreas begins sampling. Our analysis period spans mid-December 2020 to mid-February 2021. During this time there are two breaks in the measurements. On 24th December the repeatability began to deteriorate as was seen in both the ST measurements (sample loaded straight into spectrometer) and in the BT measurements, indicating an issue with the spectrometer rather than the sampling and preconcentration. The spectrometer laser path was re-adjusted and characteristic performance of the instrument resumed. This is a highly unusual intervention that should only be required very rarely. Shortly after this, however, a hardware fault in the sampling system took the instrument offline until mid-January. Once characteristic performance resumed the instrument was taken offline for two weeks for further tests of the system and analyses (e.g. measurement of H-354 for inter-comparison with IRMS). Following this the instrument began continuous measurements from 1st February. During this period there have been no necessary changes of carrier gas, calibration, or target gases. A 40 l (water volume), 200 bar cylinder of N_2 lasts over three months, a 50 l volume 200 bar BT cylinder lasts >6 months (assuming 10 measurements a day), and the 10 l volume 100 bar synthetic PRMs last >12 months. Assuming normal operation without faults Boreas could therefore operate continuously with an optimum calibration strategy for >6 months (assuming automated changeover exists for the N_2 carrier gas or if a N_2 generator was employed). Figure 5 shows the results for $\delta^{13}C$ and δ^2H measurements from this recent period of ambient air analysis. Accurate ambient air amount fraction measurements are critical for quantitative interpretation

of the isotope ratios and our approach with Boreas is explained in the supporting information S5. The measurements of BT are also shown to illustrate the repeatability of Boreas relative to the magnitude of changes in ambient air. The standard uncertainty of δ^2H, estimated from 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 $\delta^{13}C$. Measurements of atmospheric δ^2H are not as common as $\delta^{13}C$, owing to the need to have a separate dedicated IRMS and sample preparation system for this additional (and more challenging) analysis. Simultaneous analysis of both isotopes systems using a single instrument, as illustrated, could prove highly valuable for interpretation of atmospheric CH4.
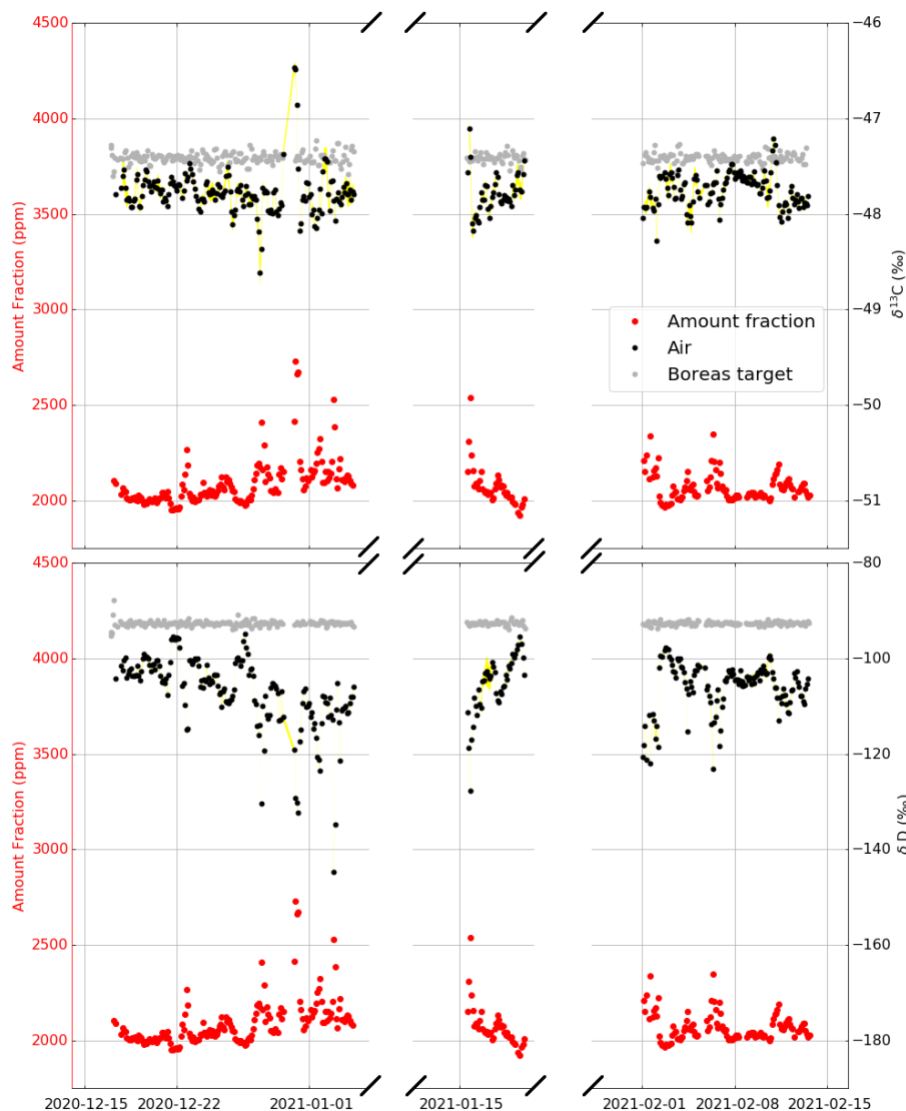

Figure 5 Boreas ambient air time series of $\delta^{13}C$ (top) and δ^2H (bottom) measurements made at NPL from a roof sampling inlet. The same offset is applied to both the BT and air measurements – in this example enabling the $\delta^{13}C$ dataset to be directly comparable to measurements by RHUL.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

5. Conclusions

We have developed an instrument able to monitor both $\delta^{13}C$ and δ^2H 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 PRMs and compressed whole-air working standards. The system is fully automated, able to make a single air measurement every 150 minutes, which is of a frequency that allows for coupling to high temporal and spatial resolution atmospheric transport models. The additional information provided through isotopic analyses could help quantitatively estimate sectoral emissions of CH_4 on country to regional scales, providing a tool for policy makers looking to make the most efficient gains in emission reductions over the coming years. Analytically there is potential for the instrument to improve further in precision and accuracy of measurement and to rival IRMS measurement as a higher specification instrument able to continuously measure more than one isotope system simultaneously and with lower maintenance cost. The performance for δ^2H is particularly favourable relative to IRMS analysis and opens up the possibility for in situ high precision global measurements of δ^2H at remote monitoring observatories.

Acknowledgements

Supporting Information

The following Supporting Information is available free of charge at the ACS website: 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

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