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A cryogen-free automated measurement system of stable carbon isotope ratio of atmospheric methane

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Abstract

Although methane plays an important role in climate change and atmospheric chemistry, its global budget remains quantitatively uncertain due mainly to a wide variety of source types. The stable carbon isotope ratio of atmospheric methane ($\delta^{13}$C-CH$_4$) is useful for separating contributions of different source categories, but due to the complex and laborious analysis, limited measurement data exists. We present a new system for $\delta^{13}$C-CH$_4$ measurement, optimized for the automated analysis of air samples. Although the system is designed in principle similarly to those in previous studies, we successfully set up the system with no use of cryogens (e.g. liquid nitrogen) and attained reproducibility sufficient to analyze atmospheric variations (~0.1 ‰). We performed automated continuous measurements of ambient air outside our laboratory at about hourly intervals for 2 months, which characterized imprint of local methane sources well. Future measurement operation for flask air samples from existing atmospheric monitoring programs will provide a large number of atmospheric $\delta^{13}$C-CH$_4$ data.

Keywords  methane; stable carbon isotope ratio; isotope ratio mass spectrometry
1 Introduction

Methane (CH₄) is an important greenhouse gas emitted from both natural and anthropogenic sources, and its removal from the atmosphere occurs primarily by the reaction with tropospheric hydroxyl radical (OH) (e.g. Saunois et al. 2016; Ito et al. 2019). Worldwide observation networks have shown the long-term, interannual, seasonal and shorter-term variations of atmospheric CH₄ mole fractions, however, many of such variations observed over the past decades still remain quantitatively unexplained (e.g. Dlugokencky et al. 2011; Cunnold et al. 2002; Bousquet et al. 2006; Morimoto et al. 2006; Schaefer et al. 2016; Nisbet et al. 2016, 2019; Rice et al. 2016; Rigby et al. 2008, 2017; Tyler et al. 2017). For effective mitigation of climate change through reduction of CH₄ emissions, an accurate understanding of various CH₄ emission processes and their magnitude and spatiotemporal variability is needed.

Stable carbon and hydrogen isotope ratio of CH₄ (δ¹³C-CH₄ and δ²H-CH₄) have been used to evaluate contributions of different CH₄ source sectors, by utilizing their source-specific isotope composition signatures and the kinetic isotope effects of removal processes from the atmosphere (e.g. Quay et al. 1999; Miller et al. 2002; Schwietzke et al. 2016). The isotope ratio δ¹³C (and similarly for δ²H) is commonly reported using the delta notation:

\[
\delta^{13}C = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1
\]  

where \(R\) represents the atomic ratio \(^{13}\text{C}/^{12}\text{C}\) in the sample or the standard. Measured
values are conventionally reported relative to the international isotope-scale VPDB (Vienna Pee Dee Belemnite). We refer to Umezawa et al. (2018) for details of the standard scale used for atmospheric $\delta^{13}$C-CH$_4$ measurements. Measurements of $\delta^{13}$C-CH$_4$ in air provide useful top-down constraints to different CH$_4$ emission categories at the global (e.g. Quay et al. 1999; Miller et al. 2002; Schaefer et al. 2016; Schwietzke et al. 2016; Nisbet et al. 2016, 2019), regional (e.g. Umezawa et al. 2012; Röckmann et al. 2016; Fujita et al. 2018), and local scales (e.g. Levin et al. 1999; Lowry et al. 2001; Zazzeri et al. 2017). It has been also suggested that interannual variations of OH have contributed to temporal trends of atmospheric CH$_4$ mole fraction and $\delta^{13}$C-CH$_4$ (e.g. Schaefer et al. 2016; Rigby et al. 2017; Tyler et al. 2017). Previous studies have examined incorporation of $\delta^{13}$C-CH$_4$ data into atmospheric chemistry transport models (e.g. Mikaloff Fletcher et al. 2004). However, given the heterogenous spatiotemporal distribution of CH$_4$ sources and their co-locations, more data to fill the data scarce regions, not only from conventional remote marine boundary layer-based stations but also from sites with substantial imprint from regional sources, are needed so as to detect signals of CH$_4$ emission changes.

Measurements of atmospheric $\delta^{13}$C-CH$_4$ has been made by offline conversion of CH$_4$ to carbon dioxide (CO$_2$) and subsequent dual-inlet isotope ratio mass spectrometry (DI-IRMS) until the 1990s (e.g. Stevens and Rust, 1982; Lowe et al. 1991; Quay et al. 1999). From the 2000s, continuous-flow isotope ratio mass spectrometry (CF-IRMS) combined with gas chromatography and a combustion furnace has become common practice (Merritt et al.
1995; Miller et al., 2002; more references in Umezawa et al. 2018). These techniques have achieved a measurement reproducibility of < 0.1 ‰. Guidelines reported by the community of atmospheric greenhouse gas observations suggest a compatibility goal of 0.02 ‰ for δ¹³C-CH₄ measurements of well-mixed background air (World Meteorological Organization (WMO) 2018), however this is still technically difficult to achieve experimentally.

Here we present a new CF-IRMS measurement system for δ¹³C-CH₄ in air installed at the National Institute for Environmental Studies (NIES). The advantage of our system is the absence of cryogens (e.g. liquid nitrogen) in all measurement steps, which enables unattended and automated operation of the system. To our knowledge, many of the earlier studies have used cryogens (e.g. liquid nitrogen) to cool preconcentration traps (e.g. Rice et al. 2001; Miller et al. 2002; Umezawa et al. 2009; Brass and Röckmann 2010; Tokida et al. 2014), and only one laboratory reported a preconcentration trap cooled by a cryogen-free compression cooler (Brand et al. 2016). Section 2 gives descriptions of our measurement set up. Section 3 presents performance data of our measurement system and section 4 our conclusions.

2 Experimental settings

Although detailed settings are different among laboratories (see Umezawa et al. 2018), preprocessing procedure of CF-IRMS measurement for δ¹³C-CH₄ can be commonly described as follows: (1) Sample air flows, or is swept by carrier helium (He), through a
preconcentration trap filled with an adsorbent maintained typically at $<-120$ °C. This step collects CH$_4$ in the sample air whilst many other gases are flushed out. (2) The preconcentration trap is heated to liberate CH$_4$ and transfer it to a cryofocusing trap. (3) The CH$_4$ released from the cryofocusing trap passes through a separation column to achieve chromatographic separation from some remaining gases. (4) The CH$_4$ is combusted to CO$_2$ (and water) in a high-temperature furnace. (5) The CH$_4$-derived CO$_2$ is further separated from co-eluted atmospheric krypton (Kr) by a post combustion separation (PCS) column. Importance of this step was recognized after Schmitt et al. (2013) (see section 3.3). (6) The CH$_4$-derived CO$_2$ is introduced to an IRMS. The following sections detail our measurement set-ups.

2.1 Overview of the system

A schematic overview of the system is shown in Fig. 1. The preconcentration and cryofocusing steps are performed by a custom-made Continuous-flow Preconcentration and Refocusing (CPR) system. CPR controls valves (V1 to V4 (FPR-ND-71-6.35-2, Fujikin Inc., Japan), 4-port Valve (A4C4WE, Valco Instruments, Co. Inc., USA), and 6-port valves A and B (A4C6WE, Valco Instruments, Co. Inc.)) and the temperatures of the two traps (T1 and T2) via a custom-made software written in DaqFactory (https://www.azeotech.com/).

CPR is equipped with three mass flow controllers (MFC1 (SEC-V110DM, HORIBA STEC, Co. Ltd., Japan), MFC2 (SEC-4400RO, HORIBA STEC, Co. Ltd.) and MFC3 (SEC-400MK3, HORIBA STEC, Co. Ltd.)) to regulate sample, standard, and ultra-high-purity He (>
99.9999%, Japan Fine Products Corp., Japan) flow through traps and the gas chromatographic (GC) section. Measurement methods of CPR (i.e. combination of valve and trap temperature settings at different steps) can be activated by receiving a trigger signal from ISODAT (software for IRMS of ThermoFisher Scientific). CPR also sends a trigger signal to the GC (Agilent 6890, Agilent Technologies, USA), which also triggers the data acquisition method of ISODAT. Accordingly, the two software programs (DaqFactory and ISODAT) run measurement methods consistently.

2.2 Sample, standard and reference gases

As shown in Fig. 1, the CPR system can introduce working standard or sample air by opening valves V1 or V3, respectively. The working standard gas is dry air containing ambient CH₄ mole fraction in a 10 L high-pressure aluminum cylinder, which was compressed to 14.7 MPa at NIES, Tsukuba. Pressurized (above ambient) sample flasks can be attached upstream of V3. MFC1 controls the flow rate of sample or standard air. The measured gas is introduced to the subsequent trap T1 after passing through Nafion tubing (Sigma-Aldrich, USA) and a chemical trap filled with Ascarite II (Thomas Scientific, USA) to remove water vapor and CO₂. We also have a pure CO₂ reference gas (> 99.995%) in a 47 L cylinder (Japan Fine Products Corp.), which is introduced into IRMS via an open split (Fig. 1). The open split is an interface between the GC section/reference gas and the IRMS. Here the incoming gas enters an open-to-atmosphere glass tube via a capirally. This tube is purged with carrier He and a constant flow rate of this gas mixture is drawn by vacuum into
the IRMS.

2.3 Preconcentration trap (T1)

The design of the preconcentration trap (T1) is schematically shown in Fig. 1. HayeSep D (80/100 mesh, 149 mg) adsorbent was packed into a section of 1/8" o.d. (2.17 mm i.d.) stainless steel tubing and secured with glass wool at both ends, and the tubing was then coiled at the packed section. This shape allows the tubing a relatively large contact area with an aluminum cold block cooled by a free piston Stirling cooler (FPSC; SC-UD08, Twinbird Corp., Japan). For temperature control, a Nichrome heating wire is wound along T1 and a temperature sensor is placed in close proximity to the packed section of the trap. The coiled trap tubing with the temperature sensor has direct surface contact to the cold block inside an insulated enclosure, which was developed based on the work by Saito and Yokouchi (2008). A cooler-based system is not disrupted by the replenishment of liquid nitrogen, and therefore has an advantage in automated and unattended operation.

In our current standard operation method, referencing Fig. 1, the upstream line of T1 is first flushed by sample (or standard) air at 10 mL min\(^{-1}\) for 3 min when V3 (or V1, respectively) is open and the 4-port Valve and 6-port Valve A are at ON (solid line) and OFF (dashed line) positions, respectively. Then 6-port Valve A is then switched to introduce sample air to T1, where CH\(_4\) in sample air is adsorbed at \(-130\) °C at a sample flow rate of 10 mL min\(^{-1}\) for 10 min (i.e. CH\(_4\) in a 100-mL sample air is collected in T1). The pressure upstream of MFC1 is kept at above ambient (controlled by a pressure regulator of the working standard air
cylinder or inner pressure of a sample flask), but we cannot precisely control local pressure
at T1 (downstream of MFC1). After that, the T1 temperature is set to 0 °C with 6-port Valves
A and B in the position OFF (dashed line), by which CH₄ adsorbed in T1 is liberated and
pushed by He carrier gas at 1.0 mL min⁻¹ (MFC2) to the refocusing trap (T2). The 6-port
Valve B is then switched to the position ON (solid line) and the temperature of T1 increased
to 30 °C to release and vent the remaining gases (e.g. CO₂, N₂O and H₂O).

2.4 Refocusing trap (T2)

After eluting from T1, the CH₄ from sample air is again trapped at the refocusing trap (T2).
This step reduces the peak width measured on IRMS and further removes N₂ and O₂. T2 is
1/16" o.d. (0.8 mm i.d.) stainless steel tubing filled with 15 mg of HayeSep D. Similarly to T1,
the low temperature of T2 is achieved by contact with a cold block cooled by an FPSC
(SC-UF01, Twinbird Corp.). In the tubing, HayeSep D was packed into a central ~5 cm
section and secured with glass wool at both ends. The HayeSep-D section of the tubing
was coiled a few times, along which Nichrome heating wire was wound and a temperature
sensor secured for temperature control. The T2 temperature is set to −140 °C for 4 min for
refocusing of CH₄ from T1, and then the temperature is increased to 30 °C to desorb the
focused CH₄ onto the GC separation column with 6-port Valve B in the position ON (solid
line) at a flow rate of 1.1 mL min⁻¹ (MFC3).

2.5 GC separations and combustion

We use a GS-CarbonPLOT column (0.32 mm ID, 30 m length, 3 μm film thickness, Agilent
Technologies, USA) for the GC separation. In the GC eluent, CH₄ is combusted to CO₂ in a combustion furnace for subsequent IRMS measurement. The conversion is achieved in alumina tubing into which braided Cuo, NiO and Pt wires are inserted (ThermoFisher Scientific). Our standard operation maintains the furnace at temperature of 940 °C as reported by Umezawa et al. (2009). The furnace is then connected to a PoraBOND Q (0.32 mm ID, 50 m length, 5 μm thickness, Agilent Technologies) column used for PCS. The two separation columns are placed in the GC oven set at 30 °C. The combustion furnace is regularly re-oxidized by introducing ultra-high-purity O₂ (> 99.99995%, Japan Fine Products). When the furnace is re-oxidized, the 6-port Valve C is switched to the position OFF (dashed line) so that O₂ gas does not flow through the PCS column, and the furnace temperature is set to 600 °C according to Sperlich et al. (2012).

2.6 Mass spectrometric measurement

After the PCS column, the CH₄-derived peak is transferred to Nafion tubing (installed in the GCC III Interface, ThermoFisher Scientific) to remove water vapor produced in the furnace and finally to the open split (housed in ConFlo IV, ThermoFisher Scientific) for introduction to an IRMS (Delta V Advantage, ThermoFisher Scientific). The IRMS measures signals for m/z = 44, 45 and 46 simultaneously. Figure 2 shows a typical chromatogram obtained for the working standard air. A peak of the CH₄, processed through the entire sample analytical line that was eventually converted to CO₂, appears at retention time ~1060 sec. Before the CH₄-derived peak, peaks of air (N₂ and O₂) and Kr origins appear at ~880 and ~970 sec,
respectively, and a peak from CO₂ in sample air that was not completely removed by the analytical line appears at \( \sim 1150 \) sec. The rectangular peaks repeated 10 times until \( \sim 600 \) sec are injections of CO₂ reference gas from the reference open split and the last peak is used for reference of the sample peak. Currently, we determine sample \( \delta^{13}C\)-CH₄ values against a \( \delta^{13}C \) value assigned for the CO₂ reference gas. The CO₂ reference gas was calibrated by dual-inlet IRMS measurements on the NIES \( \delta^{13}C\)-CO₂ scale (Mukai 2005). Our calibration strategy to reference \( \delta^{13}C\)-CH₄ measurements to the VPDB scale will be described in section 3.5.

3 Results and Discussion

3.1 Preconcentration

Complete preconcentration of CH₄ is crucial for attaining high-precision measurement of \( \delta^{13}C\)-CH₄. Earlier studies have shown that the adsorbent HayeSep D enables efficient preconcentration of CH₄ and separation from the major air component (N₂ and O₂) (Merrit et al. 1995; Eyer et al. 2014). We use HayeSep D accordingly and have tested various versions of preconcentration trap prototypes with different shapes and different amount of HayeSep D. The amount of HayeSep D in the trap determines adsorption capacity, whilst the shape of the trap is important for efficient cooling and heating of the trap, since cooling of the trap in the CPR system is achieved by contact with the cold block.

To examine preconcentration efficiency in terms of HayeSep D amount and of the trap's
shape, we made prototypes of T1 and tested them with a flame ionization detector (FID).

The FID was connected after the main separation column (replaced combustion furnace and the subsequent components of Fig. 1), which precludes uncertainty that could originate from CH$_4$ conversion to CO$_2$ in the furnace. The prototypes included those with stainless steel tubing of 1/8" and 1/16" o.d. and with HayeSep D amount approximately ranging from 20 to 120 mg. The test with various prototypes suggested that quantitative adsorption of CH$_4$ at $-130$ °C and below requires a HayeSep D amount of $> 120$ mg. In addition, contact of T1 to the cold block at larger surface area provides a more efficient and stable adsorption of CH$_4$. Thus, we currently use T1 packed with 149 mg of HayeSep D in a coil of 1/8" o.d. stainless steel tubing. We also tested a prototype with 280 mg of HayeSep D, but such further increase of HayeSep D amount did not increase the CH$_4$ peak amplitude, while it could increase the amount of interfering air components adsorbed on the trap. A possible explanation is that increased pressure inside the trap due to the enhanced flow resistance may trap larger amount of N$_2$ and O$_2$. We therefore conclude that the amount of HayeSep D packed into the trap should not be increased further, once adequate peak amplitude is achieved.

Figure 3 shows the response of the current T1 trap to the T1 setpoint temperature. We find stable $\delta^{13}$C-CH$_4$ and peak area (m/z = 44) values at $-125$ °C and below. This trap was also examined for response to sample air volume passing through T1 at $-130$ °C (Fig. 4). The peak area increases linearly with volume of sample air that passes through T1 when the...
trapping time is no longer than 18 min (i.e. sample volume of 180 mL or smaller). However, longer sample flow does not increase peak area and for trapping times of 20–50 min the peak areas are almost same, indicating partial breakthrough of CH₄. δ¹³C-CH₄ values are stable for trapping times of 7–18 min, whereas deviations occur outside of that range. The large variability for trapping times of > 20 min is due to the partial breakthrough of CH₄ corresponding to the peak area response. On the other hand, for trapping times of 5 min and shorter, δ¹³C-CH₄ clearly increases with decreasing T1 trapping time. This increase in δ¹³C-CH₄ is due to non-linearity of the IRMS. We confirmed the same magnitude of δ¹³C-CH₄ increase when the amount of reference CO₂ gas injected is reduced. A similar non-linearity trend in δ¹³C-CH₄ for small peak amplitudes was reported by Umezawa et al. (2009).

In our set up, we found that the CH₄ adsorbed on T1 can be released adequately at temperature of −80 °C and above, this temperature of CH₄ release being consistent with −85 °C reported by Brass and Röckmann (2010). Some earlier studies adopted a stepwise temperature increase of the preconcentration trap (first approximately −80 °C and finally above 0 °C), because it practically separates CH₄ from other gases adsorbed simultaneously (N₂, O₂, CO₂, N₂O and H₂O) (Umezawa et al. 2009; Brass and Röckmann 2010; Eyer et al. 2016). In this respect, we experimentally found that the peak of air (N₂ and O₂) detected on IRMS is reduced by setting the T1-to-T2 transfer temperature lower (closer to −80 °C). On the other hand, it was also found that a rapid increase of T1 temperature to
0 °C allows more efficient and stable transfer of CH$_4$ from T1 to T2 at a same transfer flow.

We avoid stepwise temperature control during the transfer, but instead we reduce the air-originated contamination peak by switching off the open split capillary (section 3.4).

Figure 5 shows how $\delta^{13}$C-CH$_4$ and peak area change with He flow rate during the T1-to-T2 transfer. The largest peak was obtained with a flow rate of 1.0 mL/min. The lower flow rate cannot transfer the CH$_4$ adsorbed on T1 completely within 4 min, and the higher flow rates indicate incomplete refocusing at T2, where the heavier isotopologue $^{13}$CH$_4$ partly breaks away. The transfer time was also optimized (not shown); with both shorter and longer times resulting in a reduced peak due to incomplete transfer and partial liberation from T2, respectively.

### 3.2 Refocusing

For refocusing of CH$_4$, previous studies have used capillary tubing cooled by liquid nitrogen (e.g. Rice et al. 2001; Umezawa et al. 2009; Tokida et al. 2014), but a recent study with a compression cooler (Brand et al. 2016) uses 1/16" o.d. stainless steel tubing as per this study. For our first attempt, we used 1/32" o.d. tubing because smaller-diameter tubing would lead to a sharper peak. However, we found inadequate CH$_4$ adsorption with 1/32" tubing. Our experiments showed that peak areas (m/z = 44) obtained from 1/32"-tubing T2 (HayeSep D 8 mg) are only half as large as those from 1/16"-tubing T2 (HayeSep D 15 mg).

Even an increased amount of HayeSep D (17 mg) in 1/32" tubing did not yield stable peak areas at temperatures of −130 °C and below, whereas 1/16"-tubing T2 achieved
quantitative adsorption at this temperature. The 1/32”- and 1/16”-tubing T2 traps with similar amounts of HayeSep D (~15 mg) are different in their shape. Since the former requires a larger length for same amount of adsorbent, it needs to be more repeatedly coiled to fit into the cold block contact configuration. It is likely that the larger diameter of the latter helps the adsorbent packing to be cooled more efficiently. It is also important to note that difference in tubing diameter changes local pressure and linear velocity inside the trap, which can considerably affect trapping of CH$_4$ and contributed to the above result.

Figure 6 shows how the CH$_4$ peak changed with T2 temperature settings. The CH$_4$ peak increases with decreasing T2 temperature and its magnitude reaches a stable value at $-130$ °C and below. The $\delta^{13}$C-CH$_4$ trend indicates incomplete trapping of heavier $^{13}$CH$_4$ at temperatures higher than $-130$ °C. Also plotted are background values of the CH$_4$ peak (m/z 46 signal just before the peak) in grey. The background values show a rapid increase with decreasing temperature below $-140$ °C. We found that the air (N$_2$ and O$_2$) peak that appears before the CH$_4$ peak (see Fig. 2) increases with decreasing T2 temperature, especially temperatures below $-140$ °C, and its tailing interferes with the CH$_4$ peak.

3.3 GC separations and combustion

As reported by Tokida et al. (2014), we confirmed that GS-CarbonPLOT achieves better separation of CH$_4$ from air (N$_2$ and O$_2$) than a PoraPLOT Q column (0.32 mm ID, 25 m, 10 μm thickness, Agilent Technologies, USA), which was widely used by previous studies (e.g. Rice et al. 2001; Umezawa et al. 2009; Brass and Röckmann 2010).
Figure 7 shows the relationship of $\delta^{13}$C-CH$_4$ and peak area with temperature of the combustion furnace. It is clearly seen in the figure that CH$_4$ combustion is incomplete at furnace temperatures below 800 °C. Such incomplete combustion yields lower $\delta^{13}$C-CH$_4$ values, indicative of isotope fractionation where lighter isotopologue $^{12}$CH$_4$ is preferentially combusted.

Re-oxidation of the furnace is carried out when frequent $\delta^{13}$C-CH$_4$ deviation of the measured value of the standard gas (typically > ~0.2 ‰ off from the nominal value) was observed and their standard deviation becomes larger (> ~0.2 ‰). This happens typically at 3 weeks or longer, and we do not observe rapid daily shifts in $\delta^{13}$C-CH$_4$ through repetitive measurements as seen by Tokida et al. (2014). The re-oxidation interval depends on how frequently the system is used for sample measurement. It was found that the system tends to provide stable measurement during periods when daily operation is continued. We empirically surmise that regular eluting of small amounts of O$_2$ contained in sample air helps condition the furnace (Miller et al. 2002). In this respect, automation of CPR is advantageous for conditioning the system constantly, since the system can be operated even during periods not used for sample analysis (e.g. nighttime).

Schmitt et al. (2013) showed that atmospheric Kr can interfere with $\delta^{13}$C-CH$_4$ measurement on IRMS. Kr is present in ambient air at ~ 1 ppm, and physicochemical separation of Kr from CH$_4$ is difficult (Schmitt et al. 2013). To eliminate the Kr interference, some laboratories have implemented a PCS column (Umezawa et al. 2018), because GC
separation of Kr from CO$_2$ (derived from CH$_4$) is easier. Brand et al. (2016) pointed out that a portion of CH$_4$ that was not combusted in the furnace could also interfere with $\delta^{13}$C measurement on IRMS, since CH$_4^+$ molecular ions formed in the ion source help CO$_2$ gas becomes protonated to CO$_2$H$^+$ (i.e. isobaric with $^{13}$CO$_2^+$). They described that un-combusted CH$_4$ should be thus separated from CO$_2$ by using a PCS column. It is noted that our PCS column (50 m) could be shorter; we achieved the necessary precision with this column along with examinations of other various component settings, but our tests indicated that columns PoraPLOT Q (0.32 mm ID, 25 m length, 5 $\mu$m thickness, Agilent Technologies) and GS-Carbon PLOT (0.32 mm ID, 30 m length, 3 $\mu$m thickness, Agilent Technologies) columns are also capable of separating Kr from CH$_4$-derived CO$_2$. The former was used by Brand et al. (2016) and the latter was used by Tokida et al. (2014), although lengths of the PCS column are different in these studies due to different settings of column temperature.

3.4 Chromatogram

A typical chromatogram shows significant intensity of the air peak (Fig. 2). We confirmed appearance of the air peak even with the combustion furnace kept at room temperature as reported by previous studies; it has been suggested that this peak is due to NO, N$_2$O and NO$_2$ produced in the ion source (Umezawa et al. 2009; Tokida et al. 2014). It is also noted that measurement of ~2 ppm CH$_4$ in N$_2$ showed a slightly reduced intensity of the air peak, which indicates that the presence of O$_2$ in sample air also plays a role. We note that the air
peak intensity is reduced (but not completely removed) by disconnecting the sample open split until 950 sec. The Kr peak was identified by analyzing ~10 ppm Kr in N₂ (10 times ambient). It is also noted that, as reported by Sperlich et al. (2013) and Brand et al. (2016), multiple injections of CO₂ reference gas are needed to condition the ion source and attain a more stable measurement. In our system, the first CO₂ peak deviates by up to ~0.5 ‰ in comparison to the last few peaks of the 10 injections.

3.5 Calibration

As described earlier, our current operation determines a sample δ¹³C-CH₄ value against a δ¹³C-CO₂ value assigned for the CO₂ reference gas (−32.460±0.007‰) injected in each measurement run. It is important that the reference CO₂ gas has a δ¹³C value close to the sample’s (about −47 ‰), otherwise measurement uncertainty could be increased due to the disparity of δ¹³C between sample and reference. The CO₂-based calibration strategy, like our current attempt, has been used by previous measurement systems (e.g. Rice et al. 2001; Morimoto et al. 2006; Umezawa et al. 2009), but we are aware that this does not follow the identical treatment principle between sample and standard (Werner and Brand, 2001) and thus cannot be free from fractionations that could occur during the entire processes in sample and reference lines and their day-to-day or longer-term variability (e.g. Miller et al. 2002). In future, we plan to assign a δ¹³C-CH₄ value to the working standard air so that the measured value for a sample can be determined against measurement of a standard that is treated in an identical manner to the sample. For this purpose, apparatus
for precise calibration of $\delta^{13}$C-CH$_4$ in the working standard, as was examined by Sperlich et al. (2012, 2016), is in preparation.

### 3.6 Reproducibility

As an indicator of reproducibility of our measurement system, Fig. 8 shows a histogram of $\delta^{13}$C-CH$_4$ deviations from the average measured value for the working standard air. The measurements of the standard air were made between 9 November 2018 and 21 January 2019 ($N$=158). The standard deviation of all the measurements is calculated to be 0.1 ‰. We also note that standard deviation from repeated working standard air measurements within one day or a couple of days is better than 0.1 ‰.

### 3.7 Automated outside air measurements

Upstream of V3, CPR has a line that draws outside air via a metal bellows pump (MB-21, Senior Metal Bellows Corp., USA) (Fig. 1). The outside air inlet is located on the roof of a one-story building at NIES. By opening V3 and continuously introducing outside air, we made automated measurements for outside air in Tsukuba for the period 9 November 2018–19 January 2019. The measurements were run mainly during the time when the system was not used for flask samples or test measurements. The measurement cycle (i.e. data interval) was ~1 hour and the standard air was analyzed at every 5 or 10 cycles. Figure 9 presents examples of measurement time-series. The CH$_4$ mole fraction for outside air samples (red) was determined by peak area in comparison to those from the standard air measurements made before and after the sample. The measurement uncertainty of CH$_4$...
mole fraction by our system is estimated to be 1.2 % (~25 ppb). The CH\textsubscript{4} mole fraction of the standard air was calibrated against laboratory CH\textsubscript{4}-in-air gases whose CH\textsubscript{4} mole fraction was determined on the NIES-94 CH\textsubscript{4} scale (Machida et al. 2008). We note that the results presented here are preliminary, but that they show an example of how our system can provide useful on-line δ\textsuperscript{13}C-CH\textsubscript{4} data.

In the course of the two-month measurements, we observed diurnal and day-to-day variations in both CH\textsubscript{4} mole fraction and δ\textsuperscript{13}C-CH\textsubscript{4}. The observed CH\textsubscript{4} mole fraction and δ\textsuperscript{13}C-CH\textsubscript{4} ranged from 1850 to 2180 ppb and −48.48 to −47.26 ‰, respectively. To depict diurnal variations, Fig. 10 shows δ\textsuperscript{13}C-CH\textsubscript{4} and CH\textsubscript{4} mole fraction as a function of time of day. It is obvious that the minimum CH\textsubscript{4} mole fraction (maximum δ\textsuperscript{13}C-CH\textsubscript{4}) was nearly constant throughout the day (approximately 1900 ppb or −47.6 ‰), while high CH\textsubscript{4} mole fraction (low δ\textsuperscript{13}C-CH\textsubscript{4}) was observed almost exclusively during nighttime to morning. In particular, we frequently observed an increase of the CH\textsubscript{4} mole fraction overnight until around 10 am accompanied by decrease of δ\textsuperscript{13}C-CH\textsubscript{4}. The nighttime CH\textsubscript{4} accumulation would be explained by build-up of the nocturnal boundary layer, and the CH\textsubscript{4} decrease afterwards would be due to formation of the daytime convective mixed layer.

To infer CH\textsubscript{4} sources contributing to the observed variations, some of the high CH\textsubscript{4} events are plotted for δ\textsuperscript{13}C-CH\textsubscript{4} as a function of the reciprocal of the CH\textsubscript{4} mole fraction (Fig. 11, often referred to as a Keeling plot). The isotope signature of the source has often been estimated by regression analysis of the Keeling plot according to the following equation (e.g.
where the respective subscripts obs, Source and BGD denote the observed, source and background CH$_4$ mole fraction C or $\delta^{13}$C-CH$_4$ values. This equation tells us that the intercept value of the regression line, obtained by plotting the observed $\delta^{13}$C-CH$_4$ values against the reciprocal of the observed CH$_4$ mole fraction, is the $\delta^{13}$C-CH$_4$ signature of the source that exchanges CH$_4$ with the overlying atmosphere. We selected two cases where clear persistent CH$_4$ increase with $\delta^{13}$C-CH$_4$ decrease was observed from evening to the following morning: 20–21 (Case 1) and 27–28 (Case 2) November. The Keeling plot analysis inferred source $\delta^{13}$C-CH$_4$ signatures of $-56.7\pm0.8$ (Case 1, $R=0.96$) and $-59.3\pm1.9$ ‰ (Case 2, $R=0.91$), these two values corresponding to microbial CH$_4$ sources (Sherwood et al. 2017). There was another event when CH$_4$ increased during the evening with $\delta^{13}$C-CH$_4$ (case 3, 22 November); the source $\delta^{13}$C-CH$_4$ signature was estimated to be $-44.7\pm1.1$ ‰ ($R=-0.70$), which is higher than those of microbial sources and rather fall within the range of fossil fuel sources (Sherwood et al. 2017). We also found 4 cases in November–December when overnight CH$_4$ increases were obvious but observed changes in $\delta^{13}$C-CH$_4$ were smaller. These events showed relatively scattered Keeling plots (not shown) and inferred source $\delta^{13}$C-CH$_4$ signatures ranging from $-46.6\pm1.4$ to $-50.1\pm3.6$ ‰. Possible nearby CH$_4$ sources are a pond in the institute garden, natural gas use in nearby
residential areas, exhaust gas from automobiles, and mixtures of these sources.

### 3.8 Flask measurements

As described earlier, when either pumped outside air or pressurized sample air stored in a flask is analyzed, the sample air comes into the system by opening V3 and it flows through MFC1, Nafion and Ascarite traps, and T1 with the 4-port Valve kept at the position ON (solid line), in reference to Fig. 1. This means that it is the pressure of the sample air itself (V3 upstream) that allows flow through T1 and preconcentration of CH$_4$ in the sample air (air-flow mode). Our system has an additional measurement mode; by opening V2 and switching the 4-port Valve to the position OFF (dashed line), carrier He gas pushes sample air in the flask and allows it to flow through T1 for preconcentration of CH$_4$ (He-flow mode).

This measurement mode is used when the internal pressure of an air sample flask is close to the ambient pressure or below. For instance, we sometimes split aliquots of air samples (originally collected at $\sim$0.15 MPa) into 100-mL sample flasks at around ambient pressure for archive, because the original sample flasks used for our air sampling networks should be routinely circulated for sample collection and measurement of various species. Such tentative archive of an air sample allows more flexibility in $\delta^{13}$C-CH$_4$ measurements. It is noted that both air-flow (Eyer et al. 2016; Brand et al. 2016) and He-flow (Rice et al. 2001; Miller et al. 2002; Brass and Röckmann 2010; Morimoto et al. 2006; Umezawa et al. 2009) modes have been used previously in continuous-flow $\delta^{13}$C-CH$_4$ measurements.

To confirm consistency of measurement results between both modes, the working standard
air was filled into 100-mL flasks and those flask samples were analyzed in He-flow mode to compare to measurements in air-flow mode. In our standard method, the standard air flows through T1 for 10 min with MFC1 set to 10 mL/min, which preconcentrates CH₄ in the gas volume of 100 mL on T1. Although this volume is equivalent to the standard air filled in a 100 mL flask at ambient pressure, our tests indicated that 10-min He flow is not sufficient to completely flush the 100-mL flask. It was found that 20-min He flushing of a sample flask is appropriate, and the measurement results are in agreement with those at air-flow mode.

For two successive days, we found differences in the measurements between both modes to be 0.05±0.10 and 0.01±0.08 ‰.

### 4 Conclusion

We set up a new measurement system for δ¹³C-CH₄ based on continuous-flow isotope ratio mass spectrometry. By using a custom-made preconcentration and refocusing trap system with Stirling coolers, our system requires no cryogen, which is highly advantageous in automated and unattended operation. Repetitive measurements indicated reproducibility of the system to be 0.12 ‰. We performed automated continuous measurements of ambient air outside our laboratory building for 2 months. The results showed clear diurnal variations of CH₄ mole fractions and δ¹³C-CH₄ with amplitudes of > 200 ppb and > 0.6 ‰, respectively, which demonstrates that the variability of such amplitudes can be well characterized by our measurement. Since our system is capable of measuring air samples stored at both above
and below ambient pressure, it is well optimized for monitoring operation using various flask
air samples collected by existing air sampling networks. Future measurement operation will
provide a number of atmospheric $\delta^{13}$C-CH$_4$ data to the atmospheric science community.

Accurate calibration of the standard air is our future task.

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List of Figures

Fig. 1  A schematic overview of the CPR-GC-IRMS system. The sub-system CPR is surrounded by the dotted square. The on/off valves V1 to V4, 4-port Valve and 6-port Valves A and B are controlled pneumatically by CPR. Solid and dashed lines of the switching valves are respectively referred to as positions ON and OFF in the text. MFC: mass flow controller, FPSC: free piston Stirling cooler, IRMS: isotope ratio mass spectrometer.

Fig. 2  (a) Typical chromatogram for a measurement of the 100-mL working standard air. Black, blue and red solid line represents peak intensity of m/z 44, 45 and 46, respectively. Rectangular peaks repeated 10 times until ~600 sec are reference CO₂ gas peaks from the reference open split. The CH₄-derived CO₂ peak (denoted as CH₄) appears at ~1060 sec. (b) A zoom-in of (a) for retention time around the CH₄-derived CO₂ peak. Denoted are gases that appear in the chromatogram and should be sufficiently separated from the CH₄ peak.

Fig. 3  δ¹³C-CH₄ (closed circles, left axis) and peak area (m/z = 44, open circles, right axis) relationships as a function of T1 temperature.

Fig. 4  δ¹³C-CH₄ (closed circles, left axis) and peak area (open circles, right axis) relationships as a function of time during the preconcentration step at T1. Corresponding sample air volume is shown on the top axis.

Fig. 5. δ¹³C-CH₄ (closed circles, left axis) and peak area (open circles, right axis)
relationships against carrier He flow rate when CH₄ in sample air is transferred from T1 to T2.

Fig. 6 δ¹³C-CH₄ (closed circles, top left axis), peak area (open circles, right axis) and background (BGD) value of CH₄-derived peak for m/z 46 (grey open squares, bottom left axis) as a function of T2 temperature.

Fig. 7 δ¹³C-CH₄ (closed circles, left axis) and peak area (open circles, right axis) relationships as a function of combustion furnace temperature.

Fig. 8 A histogram of δ¹³C-CH₄ deviations from the average for a standard air measured during 9 November 2018–21 January 2019 (N=158).

Fig. 9 Time series of δ¹³C-CH₄ measurements (blue, upper left axis) for air outside the NIES building, Tsukuba. For reference, CH₄ mole fractions determined by peak area are also shown (red, lower left axis).

Fig. 10 Diurnal variations of δ¹³C-CH₄ (blue, upper left axis) and CH₄ mole fraction (red, lower left axis) for air outside the NIES building, Tsukuba.

Fig. 11 A scatterplot of δ¹³C-CH₄ as a function of reciprocal of the CH₄ mole fraction for 3 cases during the observation period (Case 1 in blue, Case 2 in light blue and Case 3 in red). Solid line is the least-square linear regression applied for each case.
Fig. 1  A schematic overview of the CPR-GC-IRMS system. The sub-system CPR is surrounded by the dotted square. The on/off valves V1 to V4, 4-port Valve and 6-port Valves A and B are controlled pneumatically by CPR. Solid and dashed lines of the switching valves are respectively referred to as positions ON and OFF in the text. MFC: mass flow controller, FPSC: free piston Stirling cooler, IRMS: isotope ratio mass spectrometer.

Fig. 2  (a) Typical chromatogram for a measurement of the 100-mL working standard air.
Black, blue and red solid line represents peak intensity of m/z 44, 45 and 46, respectively.

Rectangular peaks repeated 10 times until ~600 sec are reference CO\textsubscript{2} gas peaks from the reference open split. The CH\textsubscript{4}-derived CO\textsubscript{2} peak (denoted as CH\textsubscript{4}) appears at ~1060 sec. (b) A zoom-in of (a) for retention time around the CH\textsubscript{4}-derived CO\textsubscript{2} peak. Denoted are gases that appear in the chromatogram and should be sufficiently separated from the CH\textsubscript{4} peak.

Fig. 3 $\delta^{13}$C-CH\textsubscript{4} (closed circles, left axis) and peak area (m/z = 44, open circles, right axis) relationships as a function of T1 temperature.
Fig. 4 δ¹³C-CH₄ (closed circles, left axis) and peak area (open circles, right axis) relationships as a function of time during the preconcentration step at T1. Corresponding sample air volume is shown on the top axis.

Fig. 5. δ¹³C-CH₄ (closed circles, left axis) and peak area (open circles, right axis) relationships against carrier He flow rate when CH₄ in sample air is transferred from T1 to T2.
Fig. 6 $\delta^{13}$C-CH$_4$ (closed circles, top left axis), peak area (open circles, right axis) and background (BGD) value of CH$_4$-derived peak for m/z 46 (grey open squares, bottom left axis) as a function of T2 temperature.

Fig. 7 $\delta^{13}$C-CH$_4$ (closed circles, left axis) and peak area (open circles, right axis) relationships as a function of combustion furnace temperature.
Fig. 8  A histogram of $\delta^{13}$C-CH$_4$ deviations from the average for a standard air measured during 9 November 2018–21 January 2019 ($N=158$).

Fig. 9  Time series of $\delta^{13}$C-CH$_4$ measurements (blue, upper left axis) for air outside the NIES building, Tsukuba. For reference, CH$_4$ mole fractions determined by peak area are also shown (red, lower left axis).
Fig. 10  Diurnal variations of $\delta^{13}$C-CH$_4$ (blue, upper left axis) and CH$_4$ mole fraction (red, lower left axis) for air outside the NIES building, Tsukuba.
Fig. 11  A scatterplot of $\delta^{13}$C-CH$_4$ as a function of reciprocal of the CH$_4$ mole fraction for 3 cases during the observation period (Case 1 in blue, Case 2 in light blue and Case 3 in red). Solid line is the least-square linear regression applied for each case.