COMPOUND-SPECIFIC RADIOCARBON ANALYSIS OF ATMOSPHERIC METHANE: A NEW PRECONCENTRATION AND PURIFICATION SETUP

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ABSTRACT. Methane contributes substantially to global warming as the second most important anthropogenic greenhouse gas. Radiocarbon (^{14}C) measurements of atmospheric methane can be used as a source apportionment tool, as they allow distinction between thermogenic and biogenic methane sources. However, these measurements remain scarce due to labor-intensive methods required. A new setup for the preparation of atmospheric methane samples for radiocarbon analysis is presented. The system combines a methane preconcentration line with a preparative gas chromatography technique to isolate pure methane samples for a compound-specific radiocarbon analysis. In order to minimize sample preparation time, we designed a simplified preconcentration line for the extraction of methane from 50 L atmospheric air, which corresponds to 50 μg C as required for a reliable ^{14}C analysis of methane-derived CO_2 gas measurement with accelerator mass spectrometry (AMS). The system guarantees a quantitative extraction of methane from atmospheric air samples for ^{14}C analysis, with a good repeatability and a low processing blank. The setup was originally designed for the measurement of samples with low methane concentrations, but it can also be adapted to apportion sources from environmental compartments with high methane levels such as freshwaters or wetlands.

KEYWORDS: extraction, methane, preparative GC, radiocarbon, source apportionment.

INTRODUCTION

Since the beginning of the industrial revolution, the concentration of methane (CH_4) in the atmosphere has increased by a factor of 2.5, which is mainly due to anthropogenic emissions (Dlugokencky et al. 2011). With a mole fraction higher than 1.8 ppm, CH_4 is today the second most important anthropogenic greenhouse gas after CO_2. Although the global budget of atmospheric CH_4 is quite well constrained, individual sources remain poorly quantified and not well understood (Saunois et al. 2016). The spatial and temporal variability of CH_4 emissions from natural sources are a major hindrance to forecasting and mitigation strategies (Bousquet et al. 2006; Saunois et al. 2016), and a warming climate could alter the strength of these emissions dramatically (Dean et al. 2018).

The sources of atmospheric CH_4 are evaluated by top-down measurements and bottom-up inventories (e.g. Hiller et al. 2014; Jacob et al. 2016), but as a result of the natural variability of CH_4 emissions, these approaches usually do not agree well (Nisbet and Weiss 2010). To improve this approach, stable and clumped isotopes of methane are also widely studied, because many CH_4 sources have a specific isotopic signature (Quay et al. 1999; Stolper et al. 2015; Sapart et al. 2017).

The radiocarbon (^{14}C) content of atmospheric CH_4 is of growing interest, since it can be used as a tool for a CH_4 source apportionment (Wahlen et al. 1989; Lassey et al. 2007; Petrenko et al. 2008; Townsend-Small et al. 2012; Petrenko et al. 2017). Indeed, "contemporary" or "modern" CH_4 sources (e.g. agriculture, biomass burning) contain present-day ^{14}C levels, whereas "old" or "fossil" CH_4 sources (e.g. fossil fuels, geologic CH_4) are ^{14}C-free. Intermediate-age sources

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such as arctic lakes or peatlands can also be dated, providing valuable information about carbon dynamics in such environments (Zimov et al. 1997; Walter et al. 2006; Garnett et al. 2011). These ^{14}C measurements can be performed by accelerator mass spectrometry (AMS), but this task is challenging given the large amounts of CH_4 required and its very low concentration in the atmosphere.

Methane is usually separated from other trace gases in a stepwise process (Lowe et al. 1991; Brenninkmeijer and Röckmann 1996; Röckmann 1998; Kessler and Reeburgh 2005; Petrenko et al. 2008; Pack et al. 2015): first CO_2 is cryogenically removed, then CO is oxidized to CO_2 and also cryogenically removed, before CH_4 can finally be oxidized and isolated as CO_2 as well. Alternatively, molecular sieves or soda lime are used to scrub CO_2 (Palonen et al. 2017; Garnett et al. 2019). However, for these simplified processes, cross contamination of CO_2 from one fraction to the next remains an issue difficult to monitor and overcome (Pack et al. 2015).

Some laboratories use a preparative gas chromatography technique to separate CH_4 from CO_2 and other trace gases. This technique has been applied for stable isotope measurements of CH_4, where only small samples are necessary for such analysis (e.g. Miller et al. 2002; Bock et al. 2010; Brass and Röckmann 2010). It has also been used in combination with an AMS, for radiocarbon measurements of repeated injections of high concentration methane samples (McIntyre et al. 2013). Although a preparative gas chromatography technique warrants that pure CH_4 is measured, its application for ^{14}C measurements of atmospheric CH_4 is not straightforward as the required sample volumes are of several orders of magnitude larger for radiocarbon analysis.

Here, we present a new methane preconcentration and purification setup (MPPS) that allows the preparation of pure atmospheric CH_4 samples for ^{14}C measurements. The system combines a methane preconcentration setup (PRECON) with a purification setup which applies preparative gas chromatography to obtain pure CH_4 samples from the atmosphere (PURIF).

METHODS

Goals and Strategy

Our research aims at enabling the extraction of CH_4 from various kinds of environments (e.g. atmosphere, fresh waters and wetlands) and performing ^{14}C measurements to deepen the knowledge of CH_4 sources and the carbon cycle. The strategy adopted for the collection, preparation and radiocarbon measurements of environmental CH_4 samples is shown in Figure 1.

The procedure can be divided in four main steps: field sampling, preconcentration, purification and ^{14}C measurement. As shown by the black dashed lines in Figure 1, the possibility to measure CH_4 from aquatic and terrestrial environments will be implemented soon. However, the system has been developed and optimized for ^{14}C measurements of atmospheric CH_4, as this task remains the biggest challenge given the low concentration of CH_4 in air (< 2 ppm) and the overwhelming presence of CO_2 (> 400 ppm). First, 50–100 L of atmospheric air is collected in an aluminum bag which is brought to the lab, where it is connected to a methane preconcentration line (PRECON), to dramatically decrease the sample size by removing CO_2 and most of the bulk air (i.e. N_2, O_2 and Ar). The preconcentrated sample is then transferred to a GC column, where CH_4 is chromatographically purified and subsequently trapped as pure CH_4. The purity can be
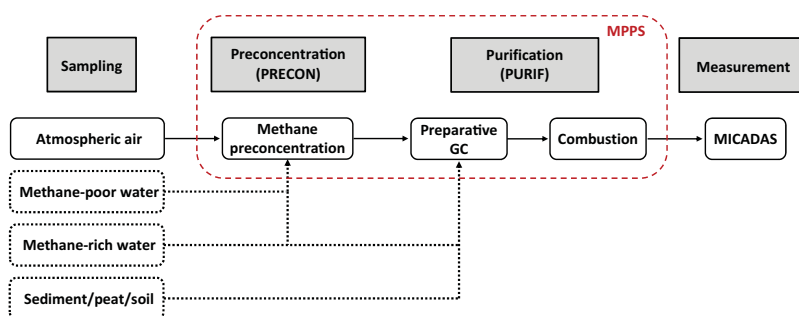
Figure 1   Strategy for $^{14}CH_4$ measurements. Red dashed box: methane preconcentration and purification setup (MPPS), which represents the essential part of this work. Black dotted line: connection of samples from other CH_4 sources that will be measured in the future. (Please see electronic version for color figures.)

checked by re-injection of the trapped CH_4 into the GC. It is then combusted to CO_2, manometrically quantified and flame-sealed in a glass ampoule. Finally, the ^{14}C measurement of the CH_4-derived CO_2 is performed with a MICADAS AMS (Szidat et al. 2014).

The individual steps involved in a ^{14}C measurement of atmospheric CH_4 are described in the following subsections, with a special emphasis on the PRECON and the PURIF analytical setups.

Sampling

It is necessary to extract CH_4 from 50–100 L of air, as its concentrations are less than 2 ppm in atmospheric background air and the target amount for reliable ^{14}C gas measurements is 50 µg C. Therefore, atmospheric air samples are collected by pumping 50-100 L air (STP) into an aluminum bag (100 L PE-AL-PE, Tesseraux, Germany) using a small membrane pump (N838ANE, KNF, Germany).

Methane Preconcentration Setup (PRECON)

Description

A new methane preconcentration setup was developed in our laboratory. It facilitates a drastic reduction of the size of atmospheric air samples from 50–100 L down to 10–15 mL by removing most of the bulk air and CO_2, while preserving the original CH_4 content. This setup (see Figure 2a) is coupled to a methane purification setup (see Figure 2b), which will be described in the next section. The main components are three cryogenic traps cooled to liquid nitrogen temperature (–196ºC), of which the first (Russian doll trap, RDT) removes CO_2, while the second (charcoal trap, CT1) and the third (CT2) allow two successive CH_4 preconcentration steps.

The line consists of 1/4" stainless steel (SS) tubing with Swagelok connections (Swagelok, USA) and a central part between V2 and V7 made of 12 mm OD glass with grease-free Rotulex joints. These two parts are connected using Ultra-Torr (UT) fittings on the glass side and SS tube adapters on the metal side (Swagelok, USA). The gas flow rates in the line, all given in normal conditions (1013 mbar, 0ºC), are regulated by two mass flow controllers MFC1 (SLA5850S, 0–5 L min^{-1}, Brooks, USA) and MFC2 (SLA5850S, 0–150 mL min^{-1}, Brooks,
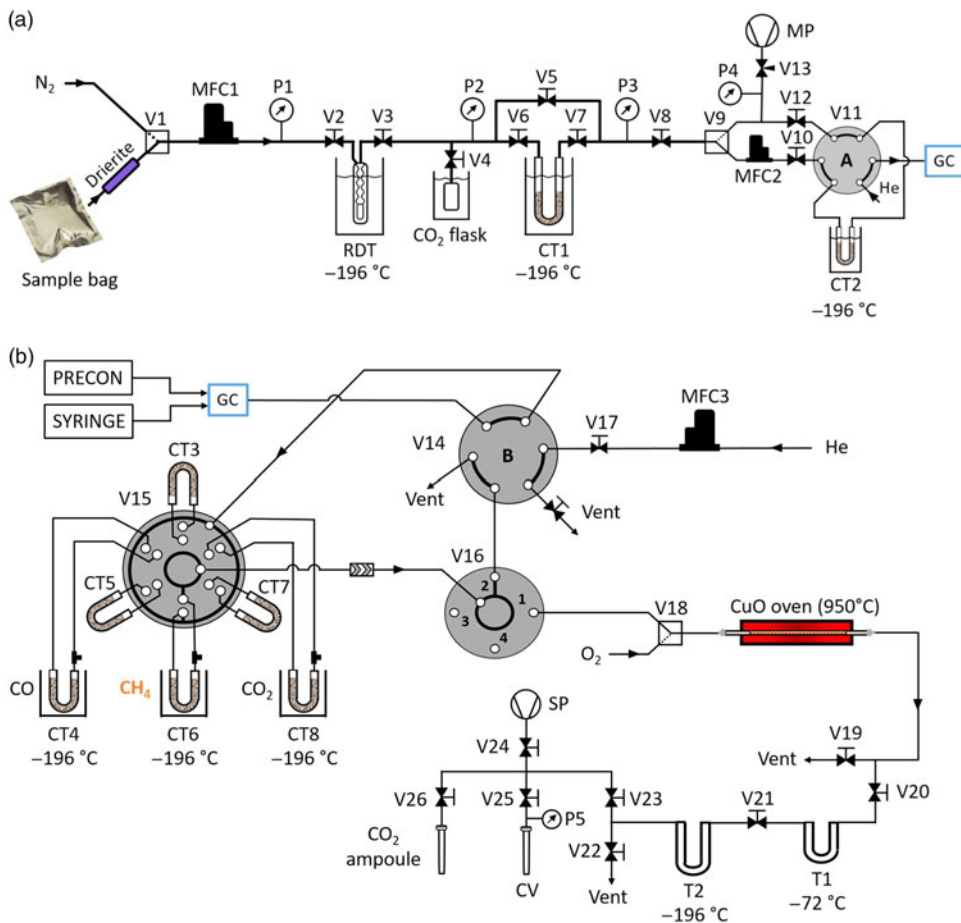
Figure 2   (a) Methane preconcentration setup (PRECON). The traps RDT, CT1 and CT2 are used for CO_2 removal, first and second CH_4 preconcentration steps, respectively. (b) Methane purification setup (PURIF), shown when trapping pure CO, CH_4 and CO_2 provided from either a syringe injection or the PRECON.

USA). MFC1 and MFC2 regulate the flow for the first and second preconcentration step, respectively. The absolute pressure along the line is monitored by four pressure sensors (P1–P3: PBMN Industrial Low Pressure, 0–2 bar; P4: PBMN flush, 0–2 bar, Baumer, Switzerland).

An aluminum bag (sample bag), which contains an atmospheric air sample collected in the field, is connected to the preconcentration line. The sample is dried in the trap "Drierite," a plastic tube (24 mm ID, L = 160 mm) filled with 70 g of Drierite™ ($CaSO_4$, 10–20 mesh, Sigma-Aldrich, USA) which turns from blue to pink when it should be regenerated (60 min, 210°C). V1 allows to switch to a nitrogen supply to clean the system (N_2, purity = 99.999%, Carbagas, Switzerland).

RDT is a custom-made "Russian doll" glass trap of a concentric design, similar to the one described by Brenninkmeijer and Röckmann (1996). When immersed into liquid nitrogen, the undulations of its inner part and three nested glass fiber thimbles (Whatman 33 × 94 mm

and 25 × 100 mm, GE Healthcare, USA) at its bottom section ensure a very efficient trapping of CO_2 and other lower volatility gases through the mechanisms of condensation and adsorption. This configuration allows an efficient removal of substantial amounts of CO_2 at high flow rates. Atmospheric CO_2, which has been scavenged from the air sample and trapped in RDT, can be recovered after the end of the preconcentration by cryogenically transferring it into the glass bottle "CO_2 flask." An automated graphitization equipment (Němec et al. 2010) is then used for the production of solid targets for $^{14}CO_2$ measurements.

CT1 is a custom-made U-shaped glass trap (13 mm ID) filled with 12 g activated charcoal (Fluka 05112, grain size 0.3–0.5 mm, 0.41 g/cm^3, Sigma-Aldrich, USA). P2 and P3 are used to monitor the pressure drop across the trap and the stability of the system throughout the first preconcentration step. A bypass allows excluding this trap from the flow path when necessary.

The second CH_4 preconcentration step is achieved in CT2, a custom-made 1/8" OD SS U-shaped trap (2.16 mm ID, L = 40 cm) filled with 0.5 g charcoal. The trap is connected to the valve V11, an electrically actuated 2-position 6-port valve with 1/8″ fittings (VICI, USA), which is used in "load" mode when CH_4 is preconcentrated into CT2 (as shown in Figure 2a) or in "injection" mode when the sample in CT2 is transferred to the GC column of the PURIF.

The sample is pumped from the aluminum bag through the preconcentration line with a membrane pump MP (MZ 2C NT, Vacuubrand, Germany), which is well suited for the handling of high gas flow rates in the line. The pump has an ultimate vacuum of 7 mbar and is also used for cleaning purposes, as it can easily tolerate the removal of potential moisture in the line. Finally, V13 is a needle valve which allows to stop pumping the line gently when required.

Procedure
Cleaning
Before the preconcentration of an air sample, the line and particularly the traps are cleaned thoroughly to remove any contamination from the previous sample or from eventual leaks in the line. First, RDT is cleaned at 95ºC (hot water bath) in a N_2 flow of 1.5 L min^{-1} for 3 min, to remove water vapor and other condensable gases that could remain adsorbed onto the glass fiber thimbles. In this step, CT1 is bypassed and the impurities are directly removed by the pump. As CT1 contains a significant amount of charcoal, care is taken to ensure that CH_4 previously adsorbed is comprehensively eliminated. To do so, CT1 is heated to 95ºC, evacuated for 10 min and then flushed with N_2 (20 min, 1.5 L min^{-1}). The trap is then pressurized to slightly above ambient pressure with N_2 and closed. Finally, CT2 is heated to 95ºC and evacuated for 3 min, flushed for three additional minutes with 50 mL min^{-1} N_2, pressurized to ~1.2 bar and closed.

First Preconcentration
A N_2 flow of 1.5 L min^{-1} is established in the line with CT1 bypassed and V9 positioned toward the pump. The sample bag is then opened and V1 is switched to connect the sample to the line. RDT is cooled to –196ºC to scrub CO_2, and after 1 min, CT1 is included into the flow path by cooling it to –196ºC, opening its inlet (V6) and outlet (V7) and closing the bypass (V5). At that time, CT1 starts trapping CH_4 and the flow integrator of MFC1 is initiated to determine the total volume of air. During the 40 min of sample transfer at a flow rate of 1.5 L min^{-1},

the pressures in the lines are monitored (P1, P2 and P3) to avoid a pressure rise due to a leak or a shortcoming of the pump that could trigger O_2 condensation (Brenninkmeijer 1991). The pressure in the line is usually very stable, with typical values at gauges P2 and P3 of 205 mbar and 85 mbar, respectively. When the pressure at P1 drops below 200 mbar, indicating that the sample has been almost totally transferred to CT1, the inlets of RDT and CT1 are closed and V1 is switched to the N_2 bottle. CT1 is evacuated until the pressure at its outlet is stable (i.e. P3 = 10–12 mbar). The liquid nitrogen bath is then replaced by a dry ice/ethanol slurry (–72°C) for 5 min 30 sec to desorb and pump away excess air trapped together with CH_4 into CT1. As shown below, there is no loss of CH_4 when bulk air is removed from the trap at –72°C. V8 is then closed, and the dry ice/ethanol bath is replaced with an ambient temperature water bath to manometrically quantify the amount of gas still trapped in the enclosed volume delimited by V6 and V8. Typical sample volumes after the first preconcentration step are 80–100 mL, which is too high to be directly transferred to the GC column for the CH_4 purification.

Second Preconcentration

The second preconcentration step, which aims at further reducing the sample volume by removing excess air, is executed in a similar way and transfers the sample from CT1 to CT2. To do so, V9 is switched toward CT2 and the line until V8, including CT2, is evacuated. The valve to the pump V13 is then closed and CT2 is cooled to –196°C. CT1 is heated to 95°C to desorb CH_4 together with excess air and all gases are then transferred to CT2 at a flow rate of 20 mL min^{-1} (MFC2) by opening V8. When the pressure after CT2 starts rising (P4), which indicates a breakthrough of air at CT2, V13 is opened to pump away excess air. When P3 drops below 50 mbar, CT1 is flushed with 20 mL min^{-1} N_2 through CT2 for 15 min to guarantee that all the CH_4 adsorbed onto CT1 is carried to CT2. The transfer is stopped by closing V8 and CT2, still at –196°C, is evacuated for 1 min. CT2 is then heated to –72°C for exactly 1 min 30 sec to desorb and remove excess air.

Transfer to the PURIF

The preconcentrated air sample, still trapped in CT2, is carried to the GC column by first switching V11 to position B (injection), which enables the He carrier gas from the GC to flush CT2 to the column. The dry ice/ethanol bath under CT2 is then removed, the trap is heated to 95°C to comprehensively desorb CH_4 and other trapped gases and the GC run is started immediately afterwards.

Methane Purification Setup (PURIF)

Description

The methane purification setup (PURIF) is schematically shown in Figure 2b. Small (<10 mL) CH_4-containing gas mixtures are chromatographically purified and pure CH_4 subfractions are recovered as CH_4-derived CO_2 in a glass ampoule. Although the setup mainly aims at preparing pure CH_4 samples for subsequent ^{14}C analysis, this preparative GC technique allows even compound-specific radiocarbon analyses of CH_4, CO, CO_2 and eventually C_2H_6. The gas sample is first chromatographically separated before pure CH_4 is isolated in an individual trap. It is then transferred to a CuO oven where CH_4 is converted into CO_2, quantified manometrically and finally flame-sealed in a glass ampoule. The system can handle two different types of sample feed: (1) a manual syringe injection into the GC inlet (SYRINGE) and (2) an on-line injection of a preconcentrated air sample (PRECON).

The GC (7890B, Agilent, USA) is equipped with a purged packed (PP) inlet, a packed column (ShinCarbon ST 80/100, 2 mm ID, L = 2 m, Restek, USA) and a thermal conductivity detector (TCD). The PP inlet was modified such that the injection valve V11 of the PRECON was included into the flow path of the He carrier gas which feeds the inlet (see Figure 2a). The column is thus constantly flushed with He (purity = 99.999%, Carbagas, Switzerland), and the flow is regulated by the electronic pneumatic control module of the GC. Hence, the option is kept to either perform a direct syringe injection of a gas mixture through the septum of the inlet (V11 in "load" mode, as shown in Figure 2a) or to transfer a preconcentrated sample from CT2 (PRECON) to the column (V11 in position "inject"). The column was chosen for its ability to handle large injection volumes at low bleeding and high efficiency of separating permanent gases and hydrocarbons. According to the physical properties of the packing material, the gases are mainly separated according to their volatility. Therefore, bulk air (O_2, N_2 and Ar) elutes first, followed by CO, CH_4, CO_2 and finally trace gases of lower volatility. The oven is kept at 40ºC for 4 min and is then heated to 250ºC with a temperature ramp of +10ºC/min. The column is finally cleaned at 280ºC for three additional minutes. The PP inlet is operated in constant pressure mode (20 psig), which causes a gradual decrease of the He carrier gas flow rate from 14 mL min^{-1} down to 9 mL min^{-1} as the temperature of the oven rises and the He viscosity increases consequently.

All the tubing is 1/8" SS with Swagelok fittings. The exhaust of the TCD is connected to V14, a 2-position 6-port valve (VICI, USA). When V14 is in position B, as shown in Figure 2b, the gases eluting from the column are carried to V15, a 6-position selector valve (EUTA-2ST6MWE-CU, VICI, USA). The trapping consists of 6 identical custom-made 1/8" OD SS U-shaped traps (2.16 mm ID, L = 35 cm), each of which filled with 0.4 g charcoal and connected to a port of V15. Although V15 was chosen for its small internal volume, intermediary traps are used to ensure a minimal cross contamination when V15 is switched from one collecting trap to the next. Each trap is also equipped with a septum injector nut (VICI, USA) holding a 6 mm septum (TCSD, Trajan, Australia) and connected to a union tee, allowing the collection of pure CH_4 (in He) aliquots with a syringe (Pressure-Lok Series A-2, 2 ml, VICI, USA).

V16 is a 4-position dead-end selector (EUTA-2SD4MWE-CU, VICI, USA). An external He supply (V14 in position A), flow-regulated by MFC3 (SLA5850S, 0–50 mL min^{-1}, Brooks, USA) is used to either clean the 6 traps (V16 in position 2) or to transfer CH_4 to the combustion oven (V16 in position 1). The methane combustion line consists of a quartz tube (4 mm ID, L = 40 cm) filled with 5.4 g copper oxide wires (0.5 mm diameter, Elementar, Germany) in its central part and connected on both ends to the SS line by means of UT fittings. The quartz tube stands in the middle of a custom-made combustion furnace heated to 950ºC.

The recovery part, where CH_4-derived CO_2 is quantified and sealed in an ampoule, is an adaptation of the THEODORE system described by Szidat et al. (2004). T1 and T2 are helicoidally-shaped 1/8" SS lines cooled to –72ºC and –196ºC when trapping the combustion products H_2O and CO_2, respectively. The line is evacuated with a scroll pump SP (IDP-3, Agilent, USA) which allows to evacuate the line down to 1×10^{-1} mbar. The amount of CO_2 recovered after CH_4 combustion is quantified with the pressure sensor P5 (PBMN Industrial Low Pressure, 0–1 bar, Baumer, Switzerland) in the calibrated volume

(CV) of 7.94 cm^3. The CH_4-derived CO_2 is finally flame-sealed into a glass ampoule (4 mm OD, L = 6–7 cm).

Procedure

When not in use, the recovery part remains evacuated to minimize contamination and to shorten the cleaning procedure preceding a sample processing. For similar reasons, CT3 to CT8 are always kept pressurized with He. The combustion oven is gradually heated to 950ºC while flushing with 20 mL min^{-1} He. Meanwhile, the GC column is baked out to remove any potential contamination and enable the TCD to reach a stable condition. The charcoal U-traps CT3 to CT8 are flushed one by one for 3 min each, and an overpressure (1.5 bar) is applied in each trap to prevent any external contamination. Just before the sample injection, the six traps are immersed into liquid nitrogen and are again individually pressurized to 1.5 bar with He. The valve V14 is then switched to position B and V16 to position 2 (see Figure 2b), so that the gases eluting from the GC column are transferred to the selected trap.

As stated above, the purification setup can either be used as a stand-alone unit, by directly injecting a gas mixture, or together with the PRECON. In the first case, the sample is injected with a syringe through the septum of the PP inlet and the GC run is started immediately after. When used together with the PRECON, the GC method is started just after heating the second preconcentration trap CT2 to 95ºC.

CT4, CT6 and CT8 are used to trap CO, CH_4 and CO_2, respectively. The GC effluent is directed through the traps CT3, CT5 and CT7 between the peaks of the three target gases to avoid any cross contamination between the carbon-containing gases eluting from the column. The selector valve V15 is switched to the position of the chosen trap 30 s before the onset of the peak at the TCD and 45 s after the TCD signal has reached baseline to account for the transfer time between the detector and the traps (around 12 s) and to ensure a comprehensive trapping of the pure subfractions. After the elution and adsorption of CO_2 on CT8, V14 is switched to position A so that the GC flow is disconnected from the trapping part to avoid any low volatile gas eluting from the column to be adsorbed in a trap.

The six traps are heated to 95ºC to desorb CH_4, CO and CO_2, the combustion line is flushed (35 mL min^{-1} He, 2 min) to a vent (V22) and T1 and T2 are cooled down to –72ºC and –196ºC, respectively. CT6 is selected and CH_4 is combusted in a He flow of 10 mL min^{-1} for 10 min and the CH_4-derived CO_2 is trapped in T2. When the combustion is completed, remaining He in T2 is pumped away and the CH_4-derived CO_2 is manometrically quantified in the calibrated volume CV before it is flame-sealed in a glass ampoule, ready for a ^{14}C-AMS gas measurement.

Methane Preconcentration and Purification Setup (MPPS)

When the PRECON and the PURIF are used together for ^{14}C measurements of atmospheric CH_4 samples, time can be saved by handling both setups simultaneously. During preconcentration of the sample, the PURIF is started up and cleaned. If a second sample needs to be processed, the cleaning of the PRECON is started (RDT, CT1 and CT2) while the first sample is purified in the GC column. A single preconcentration followed by a purification lasts ~3 hr, two samples can be prepared for ^{14}C measurements in ~5.5 hr so that three samples may be handled in one working day.

Methane ^{14}C Measurement

The CH_4-derived CO_2 ampoules are measured using the ampoule cracker of the gas handling system of the MICADAS at the University of Bern. The precision achieved during ^{14}C measurements of CO_2 samples amounting 50–80 µg C is typically 1% for a modern sample. Two standards, a ^{14}C-free CO_2 blank and the NIST Standard Reference Material 4990C (Oxa-II, $F^{14}C = 1.3407 \pm 0.0005$), are measured before and after the samples for blank subtraction, standard normalization and correction of isotopic fractionation (Szidat et al. 2014).

RESULTS AND DISCUSSION

Optimization and Performance of the PRECON

The PRECON was tested and optimized using a "pressurized air sample" from a commercially available pressurized air bottle (C017E5R, Druckluft, Carbagas, Switzerland), with measured concentrations of 426 ppm CO_2 and 2.10 ppm CH_4. It does contain neither water vapor nor CO, as these gases were removed when atmospheric air was pressurized into the bottle. A cavity ring-down spectroscopy analyzer (G2401, PICARRO, USA) was connected to the exhaust of the membrane pump to control the concentrations of CO, CO_2, CH_4 and H_2O during the different steps of the procedure. Finally, the preconcentrated samples were transferred to the GC and the TCD was used to assess the performance of the preconcentration.

The RDT removes over 99.8% CO_2 for atmospheric air samples up to a total volume of 400 L without any CO_2 breakthrough. As the preconcentrated sample is subsequently purified in the GC column, the scavenging of CO_2 does not need to be quantitative. Hence, the usage of a single RDT is sufficient and simplifies the system operation compared to the setups from others, which apply multiple successive traps for this purpose (Wahlen et al. 1989; Brenninkmeijer and Röckmann 1996; Röckmann 1998; Kessler and Reeburgh 2005; Petrenko et al. 2008).

No measurable CH_4 breakthrough ($< 2‰$) was observed in the first preconcentration trap (CT1, 12 g charcoal, 13 mm ID) for air samples up to 200 L, corresponding to a total amount of 210 µg C (CH_4) successively trapped, which is four times the targeted sample size. During the preconcentration of larger air volumes, the trapping efficiency drops gradually over time and reaches 50% CH_4 breakthrough after 430 L air. Thus, this trap should not be used for sample sizes over 200 L, as isotopic fractionation may occur and would make eventual CH_4 stable isotope measurements useless (Wahlen et al. 1989; Kessler and Reeburgh 2005).

The dimensions of the second preconcentration trap CT2 (0.5 g charcoal, 2.16 mm ID) were chosen as a downscaling of CT1 to further remove excess air while trapping the total amount of CH_4 transferred from CT1. From an original air volume of 60 L, the sample size is typically 80–100 mL after the first preconcentration step in CT1 and 10–15 mL after the second step in CT2, corresponding to successive CH_4 enrichment factors of approximately 650 and 8, respectively. Thus, CH_4 is enriched to a concentration of 8–12‰ after the two preconcentration steps, which is in agreement with the values obtained by Bergamaschi et al. (1998) for a similar procedure. The enrichment factor is lower in CT2, which can be explained by the higher O_2/N_2 ratio in the sample in CT1 compared to the original ratio in atmospheric air. This O_2 enrichment after the first preconcentration step is due to its lower volatility compared to N_2, which causes a more efficient adsorption of O_2 onto the charcoal.

This discrimination over N_2 is further enhanced in CT2, resulting in a larger proportion of the sample trapped in CT2. However, the slightly oversized CT2 prevents any CH_4 loss during the preconcentration, and the final sample volume (10–15 mL) is still appropriate for a chromatographic separation in the GC column of the PURIF.

The performance of the PRECON was also evaluated by TCD measurements during the preconcentration of 60 L of the pressurized air sample, with known concentrations of CO, CH_4 and CO_2. The results are detailed in the next section, together with the performance of the PURIF (see Figure 3 below).

Optimization and Performance of the PURIF

Separation

The main physical parameters that influence the quality of the chromatographic separation are the carrier gas flow rate and the temperature of the oven. The GC method optimization was carried out with a standard gas mixture (79% N_2, 12% CO_2, 5% O_2, 2% CO and 2% CH_4) that contains higher concentrations of the main trace gases, as the TCD is not sensitive enough for the detection of low concentration compounds. The chromatogram of the syringe injection of 2 mL standard gas mixture, corresponding to approximately 20 µg C (CH_4), is shown in Figure 3. Methane is well separated from CO and CO_2 even when using a temperature ramp to shorten the method.

An overload of the column causes a broadening and tailing of the peaks, as the column is not designed for such large gas volumes. The effect is enhanced when larger samples are injected, which causes further peak broadening and reduced retention times. This behavior does not affect the collection of pure CH_4, as the peaks of CO, CH_4 and CO_2 are still well separated. However, it causes a poor separation of CO from bulk air, which is partially counterbalanced by the low oven temperature of 40ºC for the first 4 min of the run. Unfortunately, these two peaks start to overlap for samples bigger than 2 mL. A longer column combined with a cooling of the oven could solve this issue if ^{14}CO measurements are of interest, but it would come at the cost of an extended time for the chromatographic separation and the column cleaning. As atmospheric CO is very low in concentration and hard to separate from ambient air due to a similar volatility to O_2 (Brenninkmeijer 1993), the required modifications are currently not considered.

Figure 3 additionally shows the result of the preconcentration and chromatographic purification of 60 L of the pressurized air sample, when the PRECON and PURIF are jointly used. It should first be noticed that the retention times of the gases are 1–1.5 min longer compared to a direct injection. This is partly due to the sample transfer time between CT2 and the PP inlet, but also to a strongly reduced carrier gas flow rate when the preconcentrated sample in CT2 is heated, as it expands and creates an overpressure in the PP inlet. Fortunately, the shift of the retention times is reproducible and can be accounted for when the pure subfractions are collected in their respective traps. The sample volume after preconcentration is around 10–15 mL, resulting in a strong broadening of the bulk air peak. The TCD signal slowly drops to the baseline after the elution of O_2 and N_2, which is mainly caused by the dead volumes in the line between CT2 and the PP inlet of the GC.

The PRECON greatly decreased the amount of CO_2 from the air sample. However, the GC results show that the PURIF remains a mandatory step for getting reliable $^{14}CH_4$ results, as the
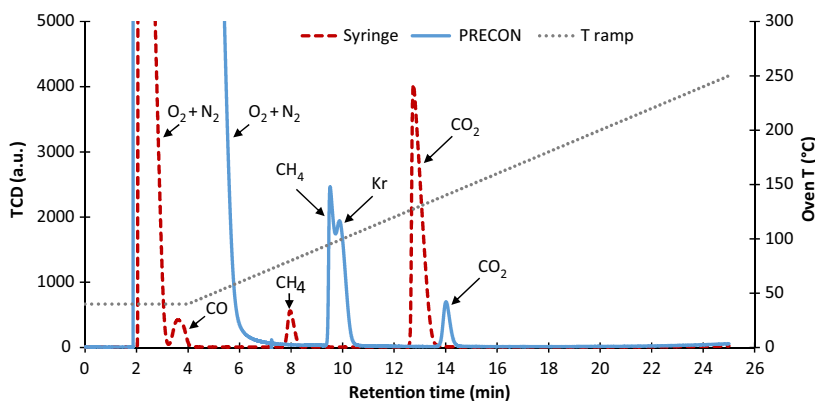
Figure 3 Chromatographic separation of a gas mixture. Dashed red line: injection into the PP inlet of 2 mL standard gas mixture (79% N_2, 12% CO_2, 5% O_2, 2% CO and 2% CH_4). Blue line: on-line injection from the PRECON of the preconcentration of 60 L pressurized air sample (2.10 ppm CH_4, 426 ppm CO_2). Grey dotted line: oven temperature program.

CO_2 amount after preconcentration is ~20% the amount of CH_4. The residual CO_2 originates from an incomplete scavenging of CO_2 in RDT along with some CO_2 production in CT1 when it is heated to 95ºC (Bräunlich 2000).

Although CH_4 is well separated from other carbon-containing gases, it unfortunately co-elutes with krypton (Kr), a noble gas that shows concentrations of ~1 ppm in the atmosphere and similar physical properties with CH_4. Since both separations in the charcoal traps of the PRECON and in the GC column are based on physical adsorption using carbon molecular sieves, Kr is preconcentrated together with CH_4 in the PRECON and co-elutes with CH_4. This issue was already documented by Schmitt et al. (2013). A full chromatographic separation may only be possible at the cost of cooling the GC oven or using a longer column, which would dramatically extend the whole procedure. As CH_4 is ultimately combusted and recovered as CO_2 in a glass ampoule, however, Kr is removed in this latter step. Consequently, co-eluting Kr impedes the ability to precisely quantify the amount of CH_4 preconcentrated, but the manometric quantification of the CH_4-derived CO_2 can still be used to assess the yield and performance of the whole procedure involving PRECON and PURIF.

Trapping

Methane trapping efficiency after its chromatographic separation was measured by connection of the outlet of the CH_4 trap (CT6) to the flame ionization detector (FID) of the GC, which is more sensitive to hydrocarbons than the TCD. Up to 2 mL pure CH_4, which corresponds to an amount of ~1000 µg C, could be trapped at –196ºC for 50 min, while the trap was flushed with a He flow rate of 35 mL min^{-1} to the FID without any detectable breakthrough. This result yields to a trapping efficiency of >99.99%.

The CH_4 trap is heated to 95ºC when CH_4 is transferred to the combustion oven. This temperature allows a comprehensive desorption of CH_4 from the charcoal and thus prevents any isotopic fractionation (Bräunlich 2000). The traps CT4 and CT8 were also successfully tested for their ability to trap and desorb CO and CO_2, respectively.

Combustion

The choice of CuO as a catalyst for the conversion of CH_4 to CO_2 was based on several aspects: it is cheap, easy to use, regenerate or replace and shows a good oxidation efficiency of hydrocarbons without any need of an additional oxidant, which simplifies the isolation of pure CH_4-derived CO_2 (Dumke et al. 1989; Kessler and Reeburgh 2005). A long and thin quartz tube allows a comprehensive combustion of CH_4 while the oven cleaning is facilitated, which minimizes cross contamination from a sample to the next. Methane combustion efficiency was assessed by connection of the outlet of T2 to the FID. As CH_4 is not trapped in T2, an empty tube cooled to –196ºC without any adsorbent, a potential incomplete combustion of CH_4 can be detected by the FID. Aiming at a time-efficient method, the highest He carrier flow granting a complete combustion of CH_4 was sought. This is achieved at a flow rate of 10 mL min^{-1} and breakthroughs of 0.2% and 1.8% are observed for flow rates of 20 mL min^{-1} and 35 mL min^{-1} He, respectively.

Validation of the MPPS

Performance

The constant contamination is a model of the procedural blank of a system (Brown and Southon 1997; Salazar et al 2015), which assumes that a constant amount of carbon with a fixed $F^{14}C$ value is added to the recovered CH_4-derived CO_2 when an air sample is preconcentrated and purified. It can be evaluated by processing CH_4 standards of known mass and ^{14}C content through the whole procedure. We use a modern methane standard that was produced through the reduction of CO_2, which was released by the combustion of tree leaves. The pure modern methane standard was measured with the MICADAS after combustion of CH_4 to CO_2 and shows a $F^{14}C$ of 1.024 ± 0.003, which is consistent with the results from the direct ^{14}C measurements of the CH_4 with gas proportional counting (GPC) at the GPC Radiocarbon Lab at the Physics Institute of the University of Bern (Loosli et al. 1980). In order to ease the handling of small volumes, the modern methane standard was diluted to 10% CH_4 in He. The CH_4 contained in the standard gas mixture was used as a fossil CH_4 standard, as it is totally depleted in $^{14}CH_4$ (i.e. $F^{14}C = 0$). Different amounts of these two gases were injected with a septum injector nut at the preconcentration line before the RDT into a N_2 flow of 60 L in total and the preconcentration and purification steps were performed as usually. The procedural blank (constant contamination) of the MPPS was determined to be 0.35 ± 0.10 µg C with an $F^{14}C$ of 0.35 ± 0.18 (see Table 1). These values were calculated using the statistical model developed by Salazar et al. (2015). The cross contamination from the previous sample, which is 0.4 ± 0.2%, most likely originates from an imperfect cleaning of the charcoal traps.

The system repeatability was determined from several preconcentration, purification and $^{14}CH_4$ measurement of 60 L pressurized air sample (see Table 1). The MPPS exhibits a good repeatability, as the standard deviation of the $F^{14}C$ for all CH_4 analyses of the pressurized air sample is 0.010, which is comparable to the average $F^{14}C$ measurement uncertainty of a single analysis (0.012). To assess the system accuracy, repeated ^{14}C measurements of the modern methane standard that was processed through the MPPS were compared to the modern methane standard $F^{14}C$ reference value. The results, presented in Table 1, show that the mean $F^{14}C$ from the repeated measurements ($F^{14}C = 1.018 ± 0.008$) is statistically indistinguishable from the reference value ($F^{14}C = 1.024 ± 0.003$). The overall yield of the setup was calculated from the comparison of the amount of CH_4-derived CO_2 recovered in a glass ampoule with its corresponding theoretical amount of CH_4 injected

Table 1 Quality assurance parameters of the Methane Preconcentration and Purification Setup (MPPS), with average uncertainty (1σ) and standard deviation (Std dev) of all measurements (both calculated referring to a single analysis). See Supplementary Materials for detailed results.

Quality parameter	Value	Uncertainty	Std dev	n
Constant contamination mass (μg C)	0.35	0.10	–	22
Constant contamination $F^{14}C$	0.35	0.18	–	22
Cross contamination (%)	0.4	0.2	–	2
Repeatability* ($F^{14}C$)	1.539	0.012	0.010	6
Accuracy#: measurement ($F^{14}C$)	1.018	0.008	0.009	3
Accuracy: reference value ($F^{14}C$)	1.024	0.003	–	–
MPPS yield (%)	101.2	1.4	–	13

*Determined from repeated analysis of 60 L of the pressurized air sample.
#Determined from repeated analysis of the modern methane standard.

into the PRECON (see Table 1). The samples used for this evaluation were collected in aluminum bags at the Beromünster tall tower, Switzerland, as described by Berhanu et al. (2017). The yield of the MPPS is 101.2 ± 1.4%, indicating a quantitative recovery of CH_4 during the preconcentration and purification steps.

The chromatographic purification of CH_4 after preconcentration is an essential step, as it guarantees the reliability of the ^{14}C results. Such an approach has been previously employed by some other groups (e.g. Wahlen et al. 1989; Eisma et al. 1994). However, their systems were used for the purification of much larger air volumes and thus required more traps and a long and labor-intensive procedure limiting their throughput. The simplified preconcentration line presented here drastically reduces the sample preparation time for a $^{14}CH_4$ measurement, as three samples can be readily prepared within a working day. Hence, the MPPS is suited to the monitoring of atmospheric $^{14}CH_4$.

Versatility

According to the research strategy depicted in Figure 1, the two systems presented in this work can be adapted to handle CH_4 collected from many diverse environments (e.g. aquatic, wetland, marine etc.), where CH_4 concentrations can be much higher than in atmospheric air. As methanogenesis is often intense in the carbon-rich sediments at the bottom of some lakes and ponds, typical concentrations in the samples collected can be high enough so that a few milliliters contain enough CH_4 for a radiocarbon analysis (Rinta et al. 2015). If so, the sample does not require preconcentration and the PURIF can be used alone as it can handle direct injections of gas mixtures up to 10 mL.

For intermediate concentration methane sources, such as arctic lakes or peatlands, gas samples are usually extracted with headspace techniques (Walter et al. 2008; Garnett et al. 2011). A methane ^{14}C analysis of such samples often involves the extraction from gas samples of a few hundred milliliters. In this case, using the whole PRECON might be an overkill; hence, it may be possible to adapt the PRECON to use the second preconcentration step with CT2 alone before performing the CH_4 purification.

Finally, CH_4 dissolved in low concentration waters can be extracted with membrane contactors (Matsumoto et al. 2013; Sparrow and Kessler 2017), resulting in extracted gas volumes similar

to the ones required for atmospheric air sampling. Thus, these samples can be handled as the atmospheric air samples by combination of the whole PRECON and the PURIF.

CONCLUSION

A new methane preconcentration and purification setup was developed for the preparation of atmospheric CH_4 samples for ^{14}C measurements. The system requires only ~50 L of atmospheric air, which can be collected in an aluminum bag or pressurized in a gas bottle. A preparative gas chromatography technique is used for CH_4 isolation, which confirms that methane has been successfully separated from any other carbon-containing gases such as CO or CO_2 that could dramatically bias the $^{14}CH_4$ results. A procedural blank of 0.35 ± 0.10 μg C with an $F^{14}C$ of 0.35 ± 0.18 was determined, which is low compared to the typical amounts of CH_4 purified and measured. Methane is quantitatively extracted from the original air sample and isolated as pure CH_4 for the AMS ^{14}C measurement, which shows a good accuracy and repeatability. The system is therefore well suited to the radiocarbon analysis of atmospheric CH_4. Since methane is not combusted before purification, CH_4 aliquots can be collected for stable isotope measurements. Combined with ^{14}C results, they should provide complementary information.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2019.76

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