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Deposited on: 13 November 2018

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ABSTRACT

Methane is the second most important anthropogenically-produced greenhouse gas, and radiocarbon analysis is extremely valuable in identifying its age and source in the environment. At the NERC Radiocarbon Facility (East Kilbride, UK) we have developed expertise in analysis of methane radiocarbon concentration and methodological approaches to field sampling over the past twenty years. This has opened a wide range of applications, which have mainly focused on: i) the age and source of methane emitted by peatlands and organic soils (e.g. to quantify the release of ancient carbon), ii) the source of aquatic emissions of methane, and iii) the age of methane generated by amenity and illegal landfill. Many of these scientifically important applications involve challenging sampling and measurement considerations, which our development programme has continually aimed to overcome. Here, we describe our current methods, and recent improvements to aid field collection of samples in remote locations. We present the results of tests which i) show the effectiveness of our methods to remove contaminants, especially CO₂, ii) quantify the radiocarbon background contribution, and iii) demonstrate the reliability of metal gas storage canisters for sample storage.

INTRODUCTION

Methane (CH₄) is a greenhouse gas with a global warming potential around twenty or more times that of carbon dioxide (CO₂) and its concentration in the atmosphere is increasing (Turner et al. 2017). Despite the major global sources of CH₄ being now largely identified, their relative contributions to the overall budget remain highly uncertain (Kirschke et al. 2013). Radiocarbon (¹⁴C) analysis offers a way to address this problem, by providing unique information on the age and source of CH₄. For example, CH₄-derived from contemporary biogenic activity contains modern ¹⁴C signatures, while detectable ¹⁴C is absent from fossil CH₄ (i.e. indistinguishable from background) due to its great age. Thus, the concentration of ¹⁴C in CH₄ has been used to determine the biogas-fraction in domestic gas supplies (e.g. Palonen et al. 2017). Moreover, measurement of the ¹⁴C content of CH₄ has provided powerful evidence on the contribution of ancient CH₄ to contemporary emissions in peatland (Cooper et al. 2017) and marine environments (Sparrow et al. 2018), giving valuable insights into how these ecosystems are responding to climate change.

At the Natural Environment Research Council (NERC) Radiocarbon Facility (East Kilbride, UK) we have been developing techniques for the radiocarbon analysis of CH₄ for over twenty years. Methods for the field collection of samples have been established for aquatic CH₄ (Garnett et al. 2016; Dean et al. 2017), together with CH₄ in the surface emissions (Garnett et al. 2012) and sub-surface layers (Garnett et al. 2011) of peatlands. Sample CH₄ concentrations can vary widely, from less than 100
ppm to tens of % CH₄. Laboratory processing of samples begins with the purification of the gas samples to isolate the CH₄ from carbon-containing contaminants; these are almost exclusively carbon dioxide in the typical sample types that we process. This step was initially undertaken using a purely cryogenic approach (Clymo and Bryant 2008) but is now achieved using soda lime (which reacts to remove CO₂) and/or zeolite molecular sieve (the zeolite adsorbs the CO₂, which can be recovered later for analysis if required; Garnett et al. 2011).

Radiocarbon analysis of CH₄ in remote locations is still challenging, particularly when the CH₄ occurs at low concentrations, and therefore requires the sampling of many litres of air to meet sample size requirements (typically a minimum of 0.5 mg CH₄-C or 1 ml CH₄ is required). Samples can be contained inside gas sampling bags (e.g. SKC foil gas bag, SKC Ltd), however, these are generally only recommended for single use, are considered unsuitable for long-term storage (the manufacturer recommends analysing the samples within 48 hrs), and are not suitable for air freight in non-pressurised cargo cabins (SKC literature, SKC Ltd). Whereas CO₂ samples can be conveniently concentrated into a small volume of adsorbent such as zeolite molecular sieve (Garnett and Murray 2013), an equivalent approach does not exist for CH₄ (Palonen et al. 2017). Molecular sieves can efficiently adsorb CH₄ when chilled (Kessler and Reeburgh 2005), but the requirement of cryogenic coolants (e.g. liquid nitrogen) means that such an approach is unlikely to be suitable for sampling in remote locations (the chilled molecular sieve also traps more abundant gases such as nitrogen, and so can be potentially hazardous; Kessler and Reeburgh 2005). A promising method is the field-conversion of sample CH₄ to carbon dioxide and subsequent trapping of the CH₄-derived CO₂ on molecular sieve (Cooper et al. 2017; Palonen et al. 2017), although the power-demands to operate a furnace in remote field locations is likely to be a limitation.

Another approach for the collection of CH₄ samples is the use of metal air sampling canisters (large glass flasks can also be used but are more fragile and vulnerable to breakage). Although more expensive than gas sample bags, they should provide considerable advantages for sampling in remote locations due to greater robustness and sample storage performance. Here, we describe our latest methods for processing CH₄ samples for radiocarbon analysis which have been adapted to facilitate the use of metal gas canisters. We also report the results of tests used to verify the methods and canisters.

**METHODS**

**Description of sample processing methods**

Prior to use, storage vessels are cleaned by evacuating to <1 x 10⁻³ mB, flooded with high purity nitrogen gas (purity 99.999 %, BOC, UK), and evacuated again to <1 x 10⁻³ mB (Edwards RV5 and RV12 Rotary Vane vacuum pumps fitted with foreline traps to prevent back migration of oil mist). Sampling is performed by using the canister’s vacuum to draw in sample gas via a hydrophobic filter (50 mm diameter PTFE membrane syringe filter, Corning, Germany) which prevents the entry of particulates and liquid water.

On return to the laboratory, sample CH₄ is recovered (as CH₄-derived CO₂) by connecting the canister to a vacuum rig (Figure 1) and first evacuating the line up to the valve on the gas canister. The rig is constructed from stainless steel vacuum tubing (6 mm o/d) and Swagelok fittings (Swagelok, USA). After isolating the vacuum pump, sample gas is introduced to the rig through a column containing...
self-indicating soda lime (Fisher Scientific, UK) which removes CO₂. The gas then passes through a column of Type 13X zeolite molecular sieve (3-4 g, 1.6 mm pellets, Sigma-Aldrich, UK) which has been prepared by heating (500 °C) and purging with nitrogen (Garnett and Murray 2013). The molecular sieve provides a secondary trap for traces of CO₂ that may have been missed by the soda lime and removes water including that generated from the CO₂ reacting with the soda lime. Connections between the canister, soda lime and molecular sieve columns are made using stainless steel and Iso-Versinic tubing (Figure 1; Saint-Gobain, France). Sample CH₄ is then combusted to CO₂ by reacting with a platinum catalyst (~8 g platinized alumina beads contained in a quartz glass tube; Johnson Mathey Chemicals, UK) heated to 950 °C (i.e. maximum temperature of the furnace), dried using a slush trap (dry ice with industrial methylated spirits; -78 °C), and the CH₄-derived CO₂ cryogenically recovered in two liquid nitrogen traps (-196 °C). The vacuum pump is used to draw sample gas from the canister through the rig (slowly at first, by only partially opening the valve to the pump), until a vacuum of ~1 x 10⁻² mB has been achieved. The recovered CO₂ is then transferred to a volume-calibrated cold finger connected to a pressure transducer and the CO₂ volume determined. In between samples the heated platinum catalyst is regenerated by flooding with high purity oxygen and then evacuated.

Tests performed to verify the reliability of the sample processing methods

Our CH₄ processing methods have previously been verified for samples that maintained a constant atmospheric pressure during processing (i.e. when supplied in foil gas bags; e.g. Garnett et al. 2012), or for relatively small gas volumes in glass flasks (~215 mL, Garnett et al. 2011). We therefore first tested whether the same rig design was suitable when processing gas volumes of greater than 2 L by replacing the gas bags with a 2.2 L glass vessel that was required to be evacuated during the processing of a sample. These initial tests were used to inform on whether the laboratory methods were likely to be reliable for 6 L metal canisters, prior to their procurement. For these tests, we pumped 8 L of outside air into a 10 L foil gas bag and used a gas-tight syringe to add a further ~100 ml of CO₂ (Air Products Ltd, UK) with a ¹³C content of ~70 %modern (see Stuiver and Polach 1977 for the definition of %modern), and ~20 ml of “fossil” CH₄ (BOC Ltd, UK) which we use as an internal laboratory background standard. The gas mixture was then transferred in aliquots into an evacuated 2.2 L glass flask and processed on the rig as described above. Three 2.2 L aliquots were processed from the same gas mixture in the 10 L bag. We chose to use atmospheric air for these tests since it would more closely simulate samples (e.g. containing water vapour), and because the relatively high CH₄ standard concentration would mean that atmospheric CH₄ would be a small fraction of the total CH₄, which we corrected for using:

\[
C_{\text{cor}} = \frac{\left( C_{\text{meas}} \times V_{\text{meas}} \right) - \left( C_{\text{atmos}} \times V_{\text{atmos}} \right)}{V_{\text{meas}} - V_{\text{atmos}}} \quad \text{(Equation 1)}
\]

Where \( C \) is the isotopic concentration (¹⁴C or δ¹³C) of the atmosphere (atmos), measured sample (meas) and sample corrected for atmospheric CH₄ (cor). \( V_{\text{meas}} \) is the total volume of CH₄-derived CO₂ recovered, and \( V_{\text{atmos}} \) the volume of atmospheric CH₂ in the sample which is calculated from the volume of the sampling vessel and assuming for atmospheric CH₂ a concentration of 1.9 ppm, a ¹³C content of 130 %modern and a δ¹³C of -47 ‰ (Lassey et al. 2007).
We next tested our methods for analysing CH₄ samples that are smaller than the minimum sample size of 0.5 mg C; this is currently the lower limit for routine samples at the NERC Radiocarbon Facility (East Kilbride). To avoid atmospheric CH₄, we created synthetic air by mixing 7 L of nitrogen gas (purity 99.999 %, BOC, UK), 1 L of oxygen (purity 99.9995%, BOC, UK) and ~100 ml of CO₂ with a ¹³C content of ~70 %modern (Air Products Ltd, UK), to which we added ~2 ml of our “fossil” CH₄ (BOC Ltd, UK) internal laboratory standard. We again transferred aliquots of this bulk gas into a 2.2 L glass flask and recovered the CH₄ component using the same methods as described above.

To test the 6 L metal canisters (6 L Silonite Canister, Entech Instruments, USA) we performed an identical test to the previous one except with slightly more CH₄ to ensure that the recovered sample was routine-sized (i.e. 6 L of gas was transferred into the canister from a foil gas bag containing 7 L nitrogen, 1 L oxygen, 100 ml CO₂ and ~4 ml ¹³C-dead CH₄). We assessed the storage performance of the 6 L metal canisters by preparing two identical standard gases containing ~5 L N₂ and ~1 L O₂ to which ~4-5 ml of ¹⁴C-dead CH₄ was directly injected into the canister using a gas-tight syringe. One sample was processed immediately, while the second was left for three months before processing (the longest amount of time that we expect to use the canisters for sample storage).

A final test was undertaken to assess the reliability of the 6 L canisters for processing non-background CH₄ samples. Relatively ¹⁴C-enriched CH₄ was obtained from a biogas plant (GBM, Bristol, UK) and stored in a pressurised cylinder. One aliquot of this gas was analysed directly through the rig (after being injected into a 1 L bag of O₂) and provided the reference value. A second aliquot was injected into a 6 L metal canister prefilled with ~5 L N₂ and ~1 L O₂ and then processed as previously.

The tests described above were used to check the reliability of the new storage and sample purification steps, in addition to the subsequent stages of routine sample processing (e.g. graphitisation). We also analysed several CH₄ standards which served as blanks to test the sample processing under optimised conditions i.e. CO₂-free and with minimal storage. These standards, which we term “CH₄ blanks” were a mix of ~5 ml ¹⁴C-dead CH₄ in ~1 L high purity O₂ that had been freshly prepared in a 1 L foil gas bag prior to being processed by directly connecting the bag to the rig.

After passing through the rig, one aliquot of CH₄-derived CO₂ from each of the routine sized (>0.5 mg C) samples was used for determining δ¹³C relative to the Vienna PDB international standard using isotope ratio mass spectrometry (IRMS; Thermo-Fisher Delta V, Germany). For all samples, an aliquot of CO₂ was converted to graphite using Fe-Zn reduction (Slota et al. 1987) and measured using accelerator mass spectrometry (AMS). Routine-sized samples were analysed at the Scottish Universities Environmental Research Centre AMS Facility (East Kilbride, UK) and smaller samples were measured at the Keck AMS Facility (UC Irvine, USA). Following convention (Stuiver and Polach 1977), radiocarbon measurements were normalised to δ¹³C of -25 ‰ and expressed as %modern, and conventional radiocarbon ages (years BP, where 0 BP = AD 1950). A laboratory background correction of 0.17 %modern was applied to the biogas ¹⁴C results, based on the long-term record for ¹⁴C-dead CH₄ standards processed in the lab. No background correction was applied to the other results. Isotope mass balance was used to calculate the mass of modern carbon (100 %modern) required to account for the deviation in ¹⁴C concentrations above zero in the samples of ¹⁴C-dead CH₄.
RESULTS

The radiocarbon concentration of routine-sized samples of $^{14}$C dead CH$_4$ recovered from 2.2 L of atmospheric air augmented with 25 ml of ~70% modern CO$_2$ ranged from 0.26±0.01 to 0.27±0.01 %modern (Table 1). Correcting for atmospheric CH$_4$ using isotope mass balance (Equation 1) reduced the $^{14}$C contents to 0.12±0.01 to 0.14±0.01 %modern (52,615±195 to 53,851±207 BP). The %modern values for these three standards were only slightly greater than for the similarly sized CH$_4$ blank processed at the same time (1).

There was a greater range in $^{14}$C content for the small CH$_4$ samples recovered from synthetic air, extending from 0.29±0.01 to 0.74±0.02 %modern (47,020 to 39,440 BP; Table 2). Although the sample with the smallest volume had the highest $^{14}$C content, the results did not suggest a strong dependency of $^{14}$C content on sample size. Furthermore, when expressed in terms of modern carbon contamination the small samples (0.8 to 2.0 μg C) had a lower contamination compared to the routine-sized samples (2.7-3.4 μg C).

The three samples of $^{14}$C-dead CH$_4$ used for testing the 6 L metal canister all gave comparable results (0.11±0.01 to 0.16±0.01 %modern; Table 3) and in terms of both $^{14}$C content and mass of modern carbon contamination were similar to the 2.2 L glass flask (Table 1; after the latter had been corrected for atmospheric CH$_4$). Although the CH$_4$ stored for 3 months in the 6 L metal canister had a slightly higher $^{14}$C content (0.16±0.01 %modern) than the reference standard that had been processed immediately (0.13±0.01 %modern), the results overlapped at <2 σ analytical uncertainty (Table 3). The biogas CH$_4$ had a $^{14}$C content that was just under 100 %modern, with the reference gas and sample processed from the canister providing identical radiocarbon concentrations (i.e. within 1 σ; Table 3).

DISCUSSION

The routine-sized (>0.5 mg C) CH$_4$ standards processed using our latest procedures all produced very good $^{14}$C results, with background-uncorrected radiocarbon ages more than 50,000 BP (Tables 1 and 3). Importantly, the %modern values for these routine-sized samples covered a narrow range from 0.11±0.01 to 0.16±0.01 %modern, demonstrating a small (1.9-3.8 μg C) but reproducible contamination that can be reliably accounted for using routine $^{14}$C background correction. Indeed, there was very little $^{14}$C difference, if any, between routine-sized samples collected in glass flasks or metal canisters, suggesting the vessels performed equally well (although we note that the relative fragility of the glass flask makes it less suitable for fieldwork). Similarly, air mixtures containing additional 70 %modern CO$_2$ were not $^{14}$C-enriched showing that the soda lime and molecular sieve traps are very effective at removing potentially contaminating CO$_2$ (Tables 1 and 3). Similar $^{14}$C concentrations have been reported by previous researchers for $^{14}$C-dead CH$_4$ samples. For example, Sparrow and Kessler (2017) reported a $^{14}$C blank of 0.23±0.07 %modern (0.24 μg C) for their CH$_4$ preparation system, and Elder et al. (2018) quantified modern $^{14}$C blank in their CH$_4$ processing apparatus to be ~1.5-2.5 μg C (which compares to 0.5-3.8 μg C for our samples). Palonen et al. (2017) measured a $^{14}$C content of 0.06±0.07 %modern for natural gas (after applying a background correction of 0.4±0.1 %modern).

The CH$_4$ sample recovered from the metal canister after 3 months storage was slightly higher in $^{14}$C content compared to an identical sample processed immediately. This might suggest limitations on
the use of these canisters for the storage of CH₄ samples. However, the ¹⁴C result for the stored CH₄ sample differed by <2 σ compared to the control canister and was similar in ¹⁴C content compared to the routine-sized glass flask samples. We therefore consider there to be insufficient evidence to suggest that the canister is unsuitable for long-term storage of CH₄ samples, and indeed, given that most of the CH₄ samples that we process are relatively young (<5000 years BP), we conclude that the storage performance of the canister is acceptable for our purposes.

The ¹⁴C %modern values of the small-sized samples were higher compared to the routine-sized samples (Table 2), indicating that further improvements are necessary to reliably date sub-millilitre CH₄ samples that are close to background. However, we note that the mass of carbon inferred from the ¹³C measurements is lower in the small-samples compared to the routine-sized. That the ¹⁴C content of the CH₄ blank was significantly lower than the other small samples might suggest incomplete removal of the 70 %modern CO₂ that was added to the latter. However, it could alternatively be derived from impurities in the N₂ that was present in the synthetic air but not the CH₄ blank.

While the results presented here support the reliability of our methods for accurate measurement of CH₄, several limitations need to be acknowledged. Firstly, though our methods reliably remove CO₂, which we believe is by far the most likely contaminant of our sample types, other contaminants could occur, albeit in far smaller quantities (such as carbon monoxide and non-CH₄ hydrocarbons e.g. ethane). It is possible that the molecular sieve used in our processing line may remove some of these contaminants if present (e.g. Rege et al. 2000). Alternatively, if the contaminants have a similar ¹⁴C content to the sample CH₄ (e.g. due to a common source) then small traces of them will not significantly change the ¹⁴C results. Nevertheless, in cases where contaminants are of concern, steps should be taken to remove them. For example, carbon monoxide can be removed using a metal catalyst (Polonen et al. 2017) or by oxidation followed by adsorption on molecular sieve (Sparrow and Kessler 2017); non-CH₄ hydrocarbons can be removed in liquid nitrogen cooled traps at 223 torr (Sparrow and Kessler 2017).

Additionally, in our trials we predominantly used ¹⁴C-dead CH₄ to assess the reliability of our methods because it is readily available and being ¹⁴C-dead provides a sensitive test for non-¹⁴C dead contaminants which we consider are most likely (e.g. atmospheric CO₂ and CH₄). To detect ¹⁴C-dead or depleted contamination would require a relatively ¹⁴C-enriched CH₄ standard. Unfortunately, to our knowledge an equivalent non-background ¹⁴CH₄ standard is not available (see also Pack et al. 2015), and hence while the CH₄ biogas that we used in our tests provided identical results for canister and non-canister processed samples, they do not provide independent verification of the true ¹⁴C content of this gas. However, using the same rig and almost identical sample processing methods we have previously demonstrated reliability of our methods; CH₄ produced from decomposing leaves in a small anaerobic digester had the same ¹⁴C content as atmospheric CO₂ in the year of collection (Garnett et al. 2016).

In our suite of tests, the δ¹³C values that we obtained for our internal laboratory CH₄ standard ranged from -46.2±0.3 to -41.5±0.3 %o for IRMS measurements. These inconsistent δ¹³C values are unlikely to be a result of contamination, otherwise we would not have achieved such reproducible and low %modern results for the same standards. Instead, isotopic fractionation seems a more likely explanation. This could have been caused by incomplete combustion of CH₄ during sample processing, although we think that this explanation is unlikely. Instead, we believe that fractionation probably occurred through not isotopically equilibrating the gas mixtures during their transfer from
the 10 L foil gas bag to the glass flask. Hence, there was a pattern whereby the first two aliquots of
the standard gases were relatively $^{13}$C-depleted, and the residual gas used for the third aliquot was
$^{13}$C-enriched (Tables 1 and 2). Which of the above explanations is correct could have been resolved
with accurate measurement of CH$_4$ yield. Unfortunately, we were unable to obtain accurate yields
because: a. preparation of the standard gases using the syringe did not allow us to accurately
determine the volume of gas used, and b. our CH$_4$ standard gas was not 100 % pure (the syringe was
cleaned by flushing with high purity oxygen and small amounts of this were progressively introduced
to the CH$_4$ standard from “dead space” within the syringe). Nevertheless, fractionation due to either
process would not impact the $^{14}$C measurements, since these were normalised according to
convention, and therefore corrected for fractionation (Stuiver and Polach, 1977). Our future
development programme will aim to identify and eliminate the cause of this isotopic fractionation.

In conclusion, the results presented here demonstrate the reliability of our methods for measuring
the radiocarbon content of CH$_4$. Tests on the 6 L metal canisters support their suitability for
collection and storage of CH$_4$ samples, which will be especially beneficial for sample collection in
remote locations. Future development will focus on further improving the quality of results with a
focus on smaller sample sizes.

ACKNOWLEDGEMENTS

We thank staff at the NERC Radiocarbon Facility and SUERC AMS Facility. We are grateful to the UK
Natural Environment Research Council for funding and to Cameron Macintyre for providing CH$_4$
standard material. We thank an anonymous reviewer for comments which led to an improvement in
the manuscript.

REFERENCES

Clymo RS, Bryant CL. 2008. Diffusion and mass flow of dissolved carbon dioxide, methane, and
dissolved organic carbon in a 7-m deep raised peat bog. Geochimica Et Cosmochimica Acta
72: 2048-2066.

contribution of permafrost carbon to methane release from thawing peatlands. Nature
Climate Change 7: 507-511.

Dean JF, Billett MF, Murray C, Garnett MH. 2017. Ancient dissolved methane in inland waters
revealed by a new collection method at low field concentrations for radiocarbon ($^{14}$C)

Czimczik CI. 2018. Greenhouse gas emissions from diverse Arctic Alaskan lakes are

Garnett MH, Gulliver P, Billett MF. 2016. A rapid method to collect methane from peatland streams
for radiocarbon analysis. Ecohydrology 9: 113-121.

methane and carbon dioxide from the profile of a raised peat bog. Radiocarbon 53: 71-83.

Garnett MH, Hardie SML, Murray C. 2012. Radiocarbon analysis of methane emitted from the

Garnett MH, Murray C. 2013. Processing of CO$_2$ samples collected using zeolite molecular sieve for


Table 1 Results for routine-sized CH₄ samples in a glass flask. Composition of the gas mixture was approximately 2.2 L outside air, 4-5 ml ¹⁴C-dead CH₄ and 25 ml of 70 %modern CO₂. ¹⁴C results presented before and after correcting for atmospheric CH₄ (δ¹³C results were unchanged following this correction).

<table>
<thead>
<tr>
<th>Publication code (SUERC-)</th>
<th>Gas mixture</th>
<th>CH₄-decorrelated CO₂ recovered (ml)</th>
<th>IRMS δ¹³CVPDB ±0.3 ‰</th>
<th>¹⁴C content (%modern ±1 σ)</th>
<th>Air-corrected ¹⁴C content (%modern ±1 σ)</th>
<th>Conventional ¹⁴C age (BP± 1 σ)</th>
<th>Background contribution (μg C)</th>
</tr>
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<tbody>
<tr>
<td>75784</td>
<td>Air+ CH₄/CO₂</td>
<td>4.50</td>
<td>-45.9</td>
<td>0.27±0.01</td>
<td>0.14±0.01</td>
<td>52,615±195</td>
<td>3.4</td>
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<td>75785</td>
<td>Air+ CH₄/CO₂</td>
<td>4.16</td>
<td>-46.2</td>
<td>0.26±0.01</td>
<td>0.12±0.01</td>
<td>53,851±207</td>
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<td>75786</td>
<td>Air+ CH₄/CO₂</td>
<td>4.66</td>
<td>-43.6</td>
<td>0.26±0.01</td>
<td>0.14±0.01</td>
<td>52,939±193</td>
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<tr>
<td>75783</td>
<td>CH₄ blank</td>
<td>5.18</td>
<td>-43.2</td>
<td>0.11±0.01</td>
<td>n/a</td>
<td>54,580±438</td>
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Table 2 Results for small-sized CH$_4$ samples in a 2.2 L glass flask. Synthetic air (high purity N$_2$ and O$_2$) was used to which was added approximately 0.5 ml $^{14}$C-dead CH$_4$ and 25 ml of 70% modern CO$_2$. NB. $\delta^{13}$C was measured by AMS on sample prepared to graphite and may not be representative of the recovered CH$_4$-derived CO$_2$.

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<tr>
<th>Publication code (UCIAMS-1)</th>
<th>Gas mixture</th>
<th>CH$_4$- derived CO$_2$ recovered (ml)</th>
<th>AMS $\delta^{13}$C$_{VPDB}$ (‰)</th>
<th>$^{14}$C content (% modern ±1 σ)</th>
<th>Conventional $^{14}$C age (BP ±1 σ)</th>
<th>Background contribution (µg C)</th>
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<td>192871</td>
<td>Synth air + CH$_4$/$CO_2$</td>
<td>0.63</td>
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<td>-32.0</td>
<td>0.23±0.01</td>
<td>48,840±260</td>
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Table 3 Testing 6 L metal canisters for collection and storage of CH$_4$ samples. Synthetic air (high purity N$_2$ and O$_2$) was used to test CO$_2$ removal and storage performance of the metal canisters (by adding $^{14}$C-dead CH$_4$ and 70 %modern CO$_2$). Two samples of relatively $^{14}$C-enriched CH$_4$ (GBM CH$_4$) were also analysed, with and without the use of the canister.

<table>
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<tr>
<th>Publication code (SUERC-)</th>
<th>Gas mixture</th>
<th>CH$_4$-derived CO$_2$ recovered (ml)</th>
<th>IRMS $\delta^{13}$C$_{VPDB}$ ±0.3 ‰</th>
<th>$^{14}$C content (%modern ±1 σ)</th>
<th>Conventional $^{14}$C age (BP ± 1 σ)</th>
<th>Background contribution (µg C)</th>
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<td>Synth air +CH$_4$/CO$_2$</td>
<td>3.29</td>
<td>-41.5</td>
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<td>77588</td>
<td>Synth air +CH$_4$ storage test GBM CH$_4$ (canister)</td>
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<td>0.16±0.01</td>
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<td>-56.7</td>
<td>98.67±0.45</td>
<td>107±36</td>
<td>-</td>
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<td>79895</td>
<td>GBM CH$_4$ (reference)</td>
<td>1.66</td>
<td>-56.6</td>
<td>97.82±0.44</td>
<td>177±36</td>
<td>-</td>
</tr>
</tbody>
</table>
**Figure 1** Schematic illustrating the processing of CH$_4$ samples on a vacuum system. LN = liquid nitrogen, IMS = industrial methylated spirits.