IMPROVED PRECISION OF RADIOCARBON MEASUREMENTS FOR CH_4 AND CO_2 USING GC AND CONTINUOUS-FLOW AMS ACHIEVED BY SUMMATION OF REPEATED INJECTIONS

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ABSTRACT. Compound specific radiocarbon measurements can be made instantaneously using a gas chromatograph (GC) combustion system coupled to a ^{14}C AMS system fitted with a gas ion source. Samples below 10 µg C can be analyzed but the precision is reduced to 5–10% because of lower source efficiency. We modified our GC for CH_4 and CO_2 analysis and injected samples multiple times to sum data and increase precision. We attained a maximum precision of 0.6% for modern CO_2 from 25 injections of 27 µg C and a background of ~0.5% (40 kyr) for ancient methane. The ^{14}C content of dissolved CO_2 and CH_4 in water samples collected at a deep-sea hydrothermal vent and a serpentine mud volcano was measured and the results for the vent sample are consistent with previously published data. Further experiments are required to determine a calibration and correction procedure to maximize accuracy.

INTRODUCTION

Compound specific radiocarbon analysis (CSRA) provides molecular-level information that can be used to identify multiple sources of carbon within an individual sample (Eglinton et al. 1996; Ingalls and Pearson 2005). Conventionally, preparative capillary gas chromatography (PCGC) or high-performance liquid chromatography (HPLC) is used to isolate individual compounds by fraction collection prior to graphitization and CSRA (Smittenberg et al. 2002; Tripp and Hedges 2004). Although high-resolution chromatographic separations can be performed, the procedure is lengthy and time consuming and careful attention is needed to minimize the introduction of extraneous carbon. Precise ^{14}C measurements are possible on samples of individual compounds containing less than 20 µg of carbon with the lower limit generally defined by the graphitization system and procedural blanks (Santos et al. 2010).

Gas ion sources (GIS) developed for ^{14}C accelerator mass spectrometry (AMS) accept CO_2 gas directly, allowing analytical instrumentation to be directly interfaced to an AMS (Middleton et al. 1989; Bronk Ramsey and Hedges 1990; Roberts et al. 2011; Fahrni et al. 2013). Routine analysis has been achieved with an elemental analyzer (EA) for bulk and compound specific samples containing 5–100 µg of carbon; however, precision is reduced due to lower source efficiency (Ruff et al. 2010). Interfaces for HPLC systems have also been developed but the elaborate apparatus has held back the implementation of this approach in ^{14}C laboratories (Liberman et al. 2004; Thomas et al. 2011).

Gas chromatographs have been interfaced to AMS systems with both hybrid-sputter and microwave-plasma type sources (Bronk Ramsey et al. 2004; Flarakos et al. 2008; McIntyre et al. 2010). The basic on-line setup follows that of stable isotope ratio mass spectrometry, in which the gas stream from the GC is passed through a combustion furnace to convert the separated compounds to CO_2 (Merritt et al. 1995). On-line AMS measurement can then be made to determine the ^{14}C content of individual compounds. To date, a variety of individual setups have resulted in similar levels of achievable sample size and precision. A single peak containing 1–10 µg can be analyzed with a precision of about ±5–10% on modern material and an ancient compound gave a ^{14}C value of about

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Fm = 0.03. Resolving power is reduced in these systems when compared with a conventional GC as ion source memory and post-column band broadening tend to increase peak widths. Nonetheless, the technique is still useful for analyzing small amounts of compounds where handling might be difficult or as a way to separate out contaminants. The reduced precision is suitable for applications such as apportionment studies in which the sources of ancient and modern carbon need to be discriminated.

Conventional graphitization and AMS can achieve a precision down to 0.2% corresponding to an error of ±15 yr on a modern sample or a limiting age >50,000 yr. This allows age dating and environmental studies to be performed with a high degree of temporal resolution. In order for GC-AMS be a viable alternative for ^{14}C analysis, the achievable precision needs to be improved. One approach that has been proposed is to perform multiple injections of the sample and sum the data (^{14}C counts) for individual peaks (Bronk Ramsey and Hedges 1995; von Reden et al. 2008). As precision is proportional to $1/\sqrt{(^{14}\text{C counts})}$, summing the data from 25 injections is expected give a 5-fold improvement in precision based on counting statistics alone. Although the amount of sample required for a single analysis is small, the total amount of sample additively required may be nearly equivalent to what is required for graphitization. However, using GC-AMS in this fashion retains several important advantages particular to on-line analysis, namely, minimizing sample handling and reducing the addition of extraneous carbon.

The aim of the study was to modify our GC-AMS system and improve the precision of CSRA measurements by performing multiple injections of a single sample and summing the data. We approached this by setting up the GC system for CH_4 and CO_2 analysis. CH_4 and CO_2 are gases of interest with respect to carbon cycling and CH_4 is not easily converted to graphite as it is a non-condensable gas. These gases can be separated rapidly by GC, with the CH_4 subsequently converted to CO_2 by combustion, and thus the 2 gases can be measured repeatedly in a short period of time. The method is applied for headspace analysis of real-world water samples collected from a sediment-covered deep-sea hydrothermal vent in the Gulf of California and a serpentine mud volcano at the Mariana Forearc.

EXPERIMENTAL

Samples

Standard gases used were instrument-grade CO_2 (modern, Fm = 1.0398 ± 0.0006, Praxair) and research-grade CH_4 (ancient, Fm = 0.0046 ± 0.0011, Corp Bros). Modern methane (Fm = 1.087 ± 0.005) was obtained from the Town of Bourne Integrated Solid Waste Management Facility, Massachusetts, USA. The modern methane was collected in 500-mL Tedlar® gas sampling bags and passed through ascarite to remove CO_2 and water. The final composition (v/v) of the modern methane was 76% CH_4, 23.5% N_2, and 0.5% O_2. A 10% mixture of modern and ancient methane was prepared in a Tedlar gas bag by mixing aliquots of the gases using a 60-mL syringe. The mixture had a ^{14}C value of Fm = 0.0883 ± 0.0009. ^{14}C Fm values were determined by analyzing the samples via conventional graphitization and AMS.

Two water samples were obtained from a deep-sea hydrothermal vent systems and a serpentine mud volcano. The hydrothermal fluid sample was collected in 2008 from the Toadstool vent at the sediment-covered oceanic spreading center in Guaymas Basin, Gulf of California (Von Damm et al. 1985). This fluid had a maximum temperature of 228 °C and its chemistry reflects extensive interaction with organic-rich sediments during hydrothermal circulation of seawater-derived hot-spring fluids. The second fluid was collected in 2009 from Ocean Drilling Program Hole 1200C drilled into a serpentine mud volcano at the South Chamorro Seamount in the Mariana Forearc (Fryer et al. 1992). The South Chamorro fluid had a measured temperature of 3 °C as it exited the drill hole. The composition of this fluid suggests derivation from the subducting slab with near seafloor modification by biogeochemical processes (Mottl et al. 2003). Fluids from both locations were collected in isobaric gas-tight samplers deployed by remotely operated vehicles (Seewald et al. 2002). Subsamples (~10 g) of the collected fluids were stored in evacuated, gas-tight 50-mL serum vials and were acidified with 1 mL 85% H_3PO_4 to liberate CO_2 prior to analysis. The Guaymas Basin sample contained 50 and 42 mmol/kg CH_4 and CO_2, respectively, and the South Chamorro sample contained 25 and 26 mmol/kg CH_4 and CO_2, respectively. The gases in the headspace were displaced with acidified water and collected in 60-mL syringes prior to analysis.

Instrumentation

Figure 1 shows a schematic of the complete system. The GC system has been described elsewhere and was modified specifically for gas analysis (McIntyre et al. 2009). A Dycor® LC100 residual gas analyzer fitted with a 1.5-m × 75-µm fused silica capillary leak was used for setup and monitoring of the GC. The GC separation was optimized using a standard gas mix (Scotty 234), which contained 5% each of CO_2, CO, H_2, CH_4, N_2, and O_2 in a balance of helium. A 6-port valve with a 54-µL sampling loop was used for sample injection and was connected via 1/16 inch stainless steel tubing to a Restek ShinCarbon ST micro-packed column (1 m × 1 mm); 54 µL of CO_2 is equivalent to 2.2 µmole and 27 µg C per injection. Hydrogen carrier was used at 4.7 mL/min and the GC oven was operated isothermally at 110 °C. The outlet of the column was connected to a 1/16 inch tee where a mixture of 2.4 mL/min oxygen and 0.37 mL/min argon was added via the side port. The outlet of the tee was connected directly to a microfurnace operated at 950 °C with a Cu/Ni/Pt 3:1:1 catalyst. The furnace was connected to a Nafion® dryer via a 0.4-mm-ID × 0.5-mm-OD stainless steel tube transfer line. The transfer line and front half of the Nafion dryer were kept at 110 °C with heater tape and insulation to maintain water as vapor. The Nafion dryer was connected to a 0.3-mm-ID glass open split via 10-cm × 250-µm fused tubing. The open split held the capillary from the AMS system and a third capillary that could be used to deliver modern CO_2 at 0.46 mL/min at specified times for normalization of the sample data. The mixture of argon from the GC (0.37 mL/min) and the modern CO_2 had a final concentration of 55% CO_2 in argon. This was used for tuning and normalization. Gases for analysis were transferred to 60-mL syringes fitted with a stopcock and injected manually into the sampling loop of the 6-port valve of the GC.

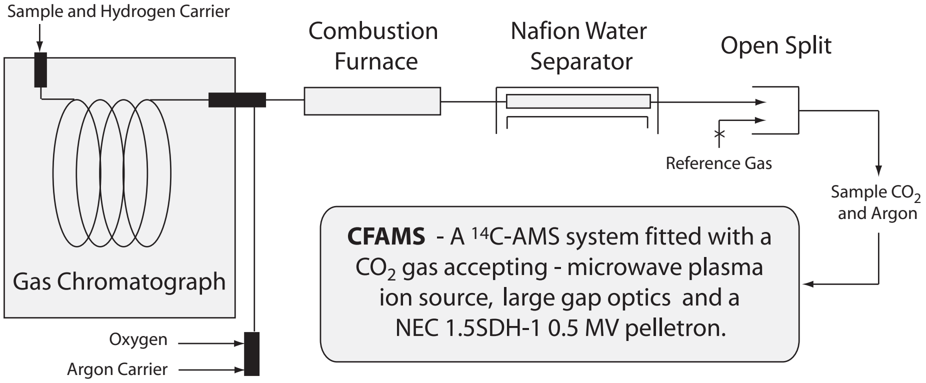

Figure 1 System schematic of the gas chromatograph continuous-flow ^{14}C AMS system

The gas chromatograph was previously set up for organic compounds such as fatty acids with a 0.53-mm × 5-µm film thickness capillary column. The column could accommodate large injection sizes of up 30 µg per compound, which was required to maximize the amount of CO_2 that was delivered to the source and maximize the precision for a single measurement. The large amounts of sample led to peak broadening, which reduced the resolving power of the system, and thick film of the column limited the maximum size of a compound that could be eluted to ~20 carbon atoms. From these characteristics, it was apparent that system would be limited to the analysis of small molecules with broad peaks. We rationalized that low molecular weight gases would be well suited to the system as they are often separated on packed columns, which result in peak widths of 10–20 s with low resolution.

The micropacked column we selected was ideal for our purpose as it operated at a carrier flow rate of 5–10 mL/min, which was suitable for the flow reduction scheme our GC employs to deliver low flow rates of argon to the AMS. The micropacked column could accommodate gas samples containing up to 30 µg per compound and it could be operated at isothermally at 110 °C. Operation at 110 °C allowed us to simplify the setup considerably. We removed the oxygen capillary in the oven that was used to keep the oxygen and hydrogen at a stoichiometric ratio during temperature-programmed operation. We replaced the transfer line between column and furnace with a simple tee and a temperature of 110 °C ensured any water present would remain in the vapor phase. Additionally, because we were analyzing gases, we removed the components that required back-flushing the solvent and connected the furnace outlet directly to the open split with a short 10-cm section fused silica. This minimized the flow path and post-column band-broadening effects.

The AMS system used has been described elsewhere (Han et al. 2007; Roberts et al. 2007, 2010, 2011). The ion source was optimized for a stable ion beam at 36-kV beam energy using 55% CO_2 in argon. A high-energy $^{12}C^+$ current of 17 µA was obtained from 300 µL/min of the normalizing gas mixture. The 3 carbon isotopes were injected into the accelerator sequentially at a rate of 10 Hz, and data from individual peaks were time-sorted and statistically combined. Fraction modern (Fm) ^{14}C values for the separated components were calculated using the ion currents for ^{12}C and ^{13}C, and ^{14}C counts. Peaks were blank-corrected and normalized to 5-min pulses of the modern reference gas. The data for individual compounds from multiple injections of a single sample were combined and the mean ^{14}C Fm value and standard deviation were calculated. The external error represents the standard error of the mean Fm value and the internal error represents the statistical error calculated from the total number of ^{14}C counts measured for each compound. The error used for the mean value was the larger of the internal and external errors.

Experiments for Precision and Isotopic Fidelity

The following 5 experiments were conducted to assess precision and isotopic fidelity:

1. The maximum precision attainable versus the number of injections was investigated for square pulses of standard CO_2 injected into the open split; 25 × 15 s pulses of modern CO_2 were injected at 1-min intervals at a concentration of 55% CO_2 in argon.
2. The precision versus the number of injections was investigated for chromatographically separated CO_2 and CH_4; 25 × 54 µL injections of 100% modern CO_2, 100% modern CH_4 and 10% modern CH_4 were made at 1-min intervals.
3. The background of the system was investigated by injecting 25 × 54 µL aliquots of ancient methane at 1-min intervals.
4. The relationship of ^{14}C Fm values with CO_2 concentration was investigated by varying the amount of standard CO_2 flowing into the open split. Pulses of 15 s and 2 min of modern CO_2

were injected into the open split at 7 flow rates, giving final concentrations of CO_2 in argon in the open split from 10 to 65%.

5. The ^{14}C value of the CH_4 and CO_2 in the headspace samples of fluids collected from deep-sea vent systems was measured by injecting 54-µL aliquots of sample every 2 min. The Guaymas Basin sample was injected 13 times and the South Chamorro sample 16 times.

RESULTS AND DISCUSSION

System Precision and Isotopic Fidelity

We studied the system precision by injecting multiple 15-s pulses of modern CO_2. We introduced the CO_2 at the open split so that the sample had the same square peak shape and gas mixture as the normalizing standard. This also ensured that minimal extraneous carbon from the GC and combustion system was introduced. A 15-s pulse width was used to approximate the width of the chromatographic peak of a single compound. Figure 2 (top) plots the individual measurements and shows that the mean value and 18 of the 25 individual measurements (72%) fall within error of the actual value obtained by conventional analysis. The standard deviation of a single individual measurement was ±2.7% which is comparable to previously obtained data for single compound measurements. Figure 2 (bottom) shows the rolling mean value and external error as it changes with injection number. It can be seen that it takes 9 injections for the mean to consistently fall within error of the actual value, and at this point the external error is ±1.4% representing a 48% improvement in precision. The final precision of ±0.54% is 5 times better than the standard deviation and is consistent with the expected improvement of $\sqrt{25}$ based on counting statistics alone. The accuracy of the measurement deviates by less than ±0.1% after 16 injections. The reasons why the final measured the value is lower than the actual value is discussed in the next paragraph. The total mass of carbon injected (672 µg) is comparable with the amount of material required for analysis via conventional AMS but larger than for off-line CSRA techniques.

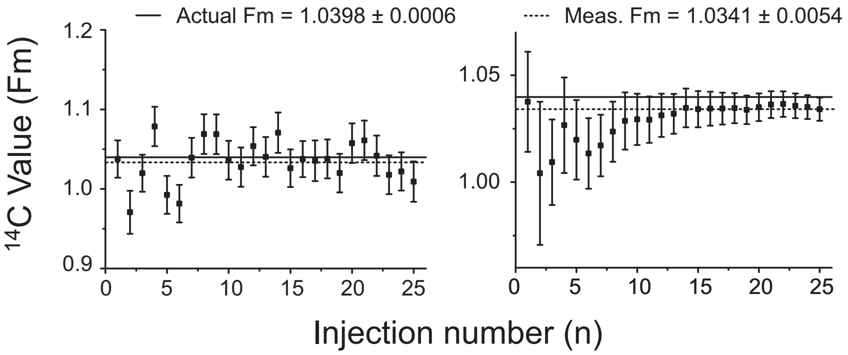

Figure 2 Maximum precision of the system. Data for 25 × 15 s pulses of the modern CO_2 injected at the open split. Top: ^{14}C Fm value of individual measurements versus injection number. The same gas mixture was used for samples and normalization. Bottom: Data plotted as a rolling mean and error.

The analysis of chromatographically separated gases was performed to study the effect of the GC and the combustion system on data. Figure 3 shows the performance of the GC using the residual gas analyzer detector. Baseline separation of the CO, CH_4, and CO_2 from H_2, O_2, and N_2 was achieved. H_2 and O_2 do not appear here as they form water and are removed by the Nafion dryer. This standard also demonstrates that the system could be used for carbon monoxide analysis. Further improvements to the system could be made at the injector as an excess of sample was used for these analyses for flushing the sampling loop prior to each injection. It should be possible to easily modify the injection port to be able to perform direct headspace extraction and reduce the ratio of the amount of sample loaded to sample injected to unity by evacuating the loop rather than flushing.

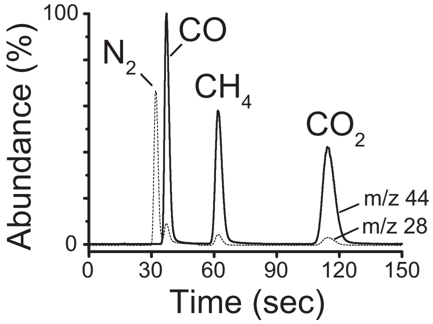

Figure 3 Chromatogram showing the optimized separation of a standard gas mixture (Scotty mix 234) recorded during set up with a residual gas analyzer. Column used is a 1-m × 1-mm ShinCarbon ST Micropacked column operating isothermally at 110 °C with hydrogen carrier gas. Baseline separation of components is also achieved in less than 2 min. ^{14}CO analysis is also possible with this configuration.

Table 1 shows the results from 4 standard gases at 20 °C. Modern CO_2 was analyzed for separation without combustion. Modern and 10% modern methane was analyzed to test the effect of the combustion system and verify isotopic fidelity. The ancient methane was analyzed to test the background. The results show that the precision from 25 injections is better than 1% for a modern sample; this is comparable to that obtained by analysis via conventional AMS methods. However, the accuracy of the measurements for the modern CH_4 and CO_2 was reduced. The mean values were 2% lower than expected. The offset may be a result of instrumental drift or by the addition of approximately 0.5 ug of GC column bleed with a value of 0.3 Fm per injection. It may also result from the fact that the peak shape and width of compounds eluting from the GC are different from that of the normalizing standard. Eluting peaks are narrower and Gaussian shaped due to the chromatographic process and this produces a dynamic change in the concentration of the CO_2 in the open split. Changes in CO_2 concentration change the viscosity and hence the flow rate of the gas entering the source, making the analysis conditions different from those used for tuning and normalization. The mean value of 10% modern gas fell within error of the actual value; however, its Fm value would not have been altered significantly by the addition of extraneous carbon if it had a similar Fm value. The ancient methane had an Fm value 0.5% higher than the actual value, which indicates that extraneous carbon is introduced by the GC system; however, this background value is substantially lower than the value of 3% that has been obtained previously.

Table 1 Radiocarbon analysis of standard gases by GC-AMS. Mean value and error for 25 injections of 54 μL of gas. Actual ^{14}C values are derived from conventional graphite analysis.

Gas	Purity (%)	Actual ^{14}C value (Fm)	Measured ^{14}C value (Fm)	C injected (μm, 20 °C)
CO_2	100	1.0398 ± 0.0006	1.0222 ± 0.0063	672
CH_4	76	1.0870 ± 0.0050	1.0656 ± 0.0074	510
CH_4	97	0.0883 ± 0.0009	0.0891 ± 0.0021	652
CH_4	100	0.0046 ± 0.0011	0.0105 ± 0.0008	672

Effect of Varying CO_2 Concentration

To further investigate the offset of our measured values, we studied the response of the system to varying concentrations of CO_2. Figure 4 shows the results of 15-s and 2-min pulses of modern CO_2

injected into the open split at concentrations of 10, 24, 40, 51, 55, 59, and 65% in argon. It can be seen that for this setup there is a dependence of the ^{14}C Fm value on the CO_2 concentration entering the source. There is a general trend that an increase in concentration leads to an increase in Fm value with mixtures containing >50% CO_2 scattered about the expected value. The 15-s pulses have an error of ±3–6% and the 2-min pulses have an error of ±1–2%, which shows that if these data were used for normalization, then any gains in precision made by multiple injections of the sample would be lost due to error propagation. The limited number of data points given here does not allow for an accurate function to be determined; however, the trend confirms that the offset in accuracy we observe in our measured values could be accounted for by the normalization process. The implication of this finding is that careful calibration and correction might be required to produce accurate results in samples with varying amounts of CO_2. The approach would be to inject multiple aliquots of the modern methane standard immediately after the sample using the same amount of carbon as the sample. The matching sample size would ensure the peak area and shapes are the same and the timing would minimize any effects from instrumental drift. The resulting data point could then be used for normalization and correction of the sample data. Multiple injections of the standard would be required to maintain the precision of the overall measurement. Taking these precautions, the system should be sufficiently accurate and precise for ^{14}C dating measurements.

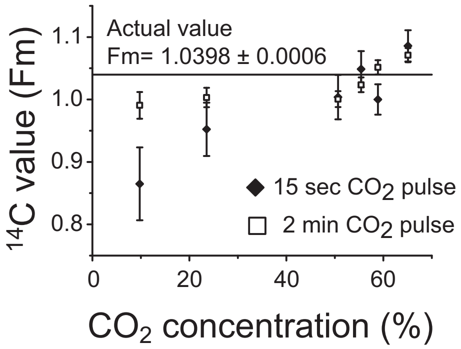

Figure 4 The effect of varying the concentration of CO_2 delivered to the source on ^{14}C Fm value. Data for 15-s and 2-min square pulses of CO_2 injected at the open split. The concentration was changed by adjusting the flow rate of CO_2 supplied at the open split.

Analysis of Water Samples from Hydrothermal Vents

The study of carbon of cycling at deep-sea hydrothermal vents has shown that CO_2 and CH_4 can be thermogenic, biogenic, and abiotic in origin (McCollom and Seewald 2007). These sources have varying contents of ^{14}C and, therefore, source apportionment studies can reveal the dominant processes taking place at a vent site. We selected water samples from 2 deep-sea systems for CSRA that contained high levels of CH_4 and CO_2. Figure 5 shows the GC-AMS chromatogram from injection of headspace gases from both samples. The samples were injected every 2 min as CH_4 elutes at 1 min and CO_2 elutes at 2 min (Figure 3). The CH_4 peak is narrower and higher than the later eluting CO_2 peak. Two samples were processed in 1 hr and with a precision comparable to data obtained from conventional AMS (Table 2). The Toadstool sample from the Guaymas Basin has ^{14}C Fm values that are consistent with those measured by conventional graphitization and AMS for an adjacent vent (Rebecca's Roost) at this location (Pearson et al. 2005). This value is consistent with derivation of CH_4 during thermal alteration of ^{14}C-poor organic-rich sediments at significant depth below the seafloor. The ^{14}C Fm value for CO_2 at Toadstool was greater than previously published values for the nearby Rebecca's Roost and likely reflects incorporation of additional modern carbon from a shallow sedimentary or seawater source. The sample from the South Chamorro Seamount had CH_4 with a ^{14}C Fm at background levels consistent with generation by abiotic and/or thermogenic processes during subduction of the down-going slab beneath the Mariana Arc. Dissolved CO_2 in the South Chamorro sample contained ~10% modern carbon, which suggests the majority was likely derived from the down going slab with the admixture of some seawater bicarbonate in near seafloor environments. The results presented here show that the technique is useful for analysis of these types of samples and that a background value of 0.5% or >40,000 yr is possible.

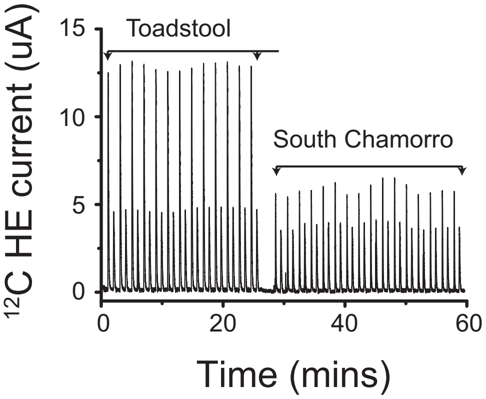

Figure 5 GC-^{14}C-AMS chromatogram of headspace gases from water samples collected at deep-sea vent systems. The Toadstool hydrothermal vent is located in the Guaymas Basin, Gulf of California, and the South Chamorro Seamount is a mud volcano located at the Mariana Forearc. For both samples, the taller first peak is CH_4 and the second is CO_2. Five-min pulses of normalizing gas bracket the samples (not shown).

Table 2 Radiocarbon analysis of dissolved gases in water samples collected at deep-sea hydrothermal vent systems.

Toadstool, Guaymas Basin		South Charmorro Seamount	
Methane (CH_4)		**Methane (CH_4)**	
Reported Fm	0.077 ± 0.001	Actual Fm	unknown
Measured Fm	0.074 ± 0.003	Measured Fm	0.005 ± 0.002
Carbon dioxide (CO_2)		**Carbon dioxide (CO_2)**	
Reported Fm	0.056 ± 0.001	Actual Fm	unknown
Measured Fm	0.076 ± 0.004	Measured Fm	0.092 ± 0.004

CONCLUSIONS

We have developed an online GC-AMS system to measure the ^{14}C content of CH_4 and CO_2. The precision of the measurements was improved to a maximum of ±0.6% for a modern sample by performing multiple injections of the sample and summing the data. The precision and sample size was comparable to that obtainable by conventional AMS, but the data was less accurate. The background from the system was ~0.5%, which is equivalent to >40,000 yr. The ^{14}C content of CH_4 and CO_2 in samples taken from a deep-sea hydrothermal vent and a serpentine mud volcano were measured and the results for the vent sample were comparable to previously published literature. Further experiments are required to determine a calibration procedure and correction factors to maximize accuracy. With this precaution, on-line compound specific ^{14}C dating of gases should be possible with satisfactory accuracy and precision.

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