A CONTINUOUS-FLOW GAS CHROMATOGRAPHY ^{14}C ACCELERATOR MASS SPECTROMETRY SYSTEM

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ABSTRACT. Gas-accepting ion sources for radiocarbon accelerator mass spectrometry (AMS) have permitted the direct analysis of CO_2 gas, eliminating the need to graphitize samples. As a result, a variety of analytical instruments can be interfaced to an AMS system, processing time is decreased, and smaller samples can be analyzed (albeit with lower precision). We have coupled a gas chromatograph to a compact ^{14}C AMS system fitted with a microwave ion source for real-time compound-specific ^{14}C analysis. As an initial test of the system, we have analyzed a sample of fatty acid methyl esters and biodiesel. Peak shape and memory was better then existing systems fitted with a hybrid ion source while precision was comparable. $^{14}C/^{12}C$ ratios of individual components at natural abundance levels were consistent with those determined by conventional methods. Continuing refinements to the ion source are expected to improve the performance and scope of the instrument.

INTRODUCTION

The development of hybrid gas-accepting ion sources for accelerator mass spectrometry (AMS) by modification of conventional Cs sputter ion sources has enabled the direct analysis of radiocarbon in CO_2 gas (Middleton 1984; Bronk and Hedges 1987; Middleton et al. 1989; Ferry et al. 1996; Hughey et al. 2000; Ruff et al. 2007). The need to graphitize samples is eliminated, thus reducing the time required for analysis and the potential for contamination. Extremely small samples can be analyzed (<1 μg C) and reasonable beam currents and ion source efficiencies are obtained. However, the total output and precision is lower than for a conventional sputter ion source; therefore, implementation of the technology for routine use has been limited to a few laboratories (Bronk Ramsey et al. 2004; Skipper et al. 2004; Synal et al. 2007; Uhl et al. 2007).

Another benefit of a gas-accepting ion source is that it allows other analytical instruments to be interfaced to an AMS system. Systems incorporating an elemental analyzer (EA) (Rottenbach et al. 2008; Szidat 2009), gas chromatograph (GC) (Hughey et al. 2000; Bronk Ramsey et al. 2004; Flarakos et al. 2008), or high-performance liquid chromatograph (HPLC) (Liberman et al. 2004; Skipper et al. 2004) have been developed permitting real-time compound-specific radiocarbon analysis (CSRA). The main challenges in these cases have largely been technical. Separated components need to be delivered to the ion source as CO_2 in a suitable flow of carrier gas, and this is achieved using a combination of combustion, cryogenic trapping, drying, gas flow splitting, and transfer steps. These are tantalizing approaches that seek to improve on conventional methods such as CSRA by preparative capillary gas chromatography (pcGC), which, when combined with graphite preparation, is a lengthy and intensive procedure (Eglinton et al. 1996; Mandalakis and Gustafsson 2003; Zencak et al. 2007). Methods utilizing graphite preparation retain the advantage of precision, while hybrid ion source techniques offer speed and molecular resolution, the latter of which is of particular interest to isotope studies in experimental medicine and earth sciences.

In terms of chromatography, it is generally considered that the main drawback of a hybrid ion source is a memory inherent to the process by which CO_2 is converted to C^- ions. The exact mechanism of conversion is not clear; however, adsorption of the CO_2 with subsequent sputtering has been pro-

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posed (Bronk and Hedges 1987). Whatever the case, noticeable time periods are observed where the signal decays after CO_2 has stopped flowing (Bronk Ramsey and Hedges 1995). Careful design of the cathode geometry and gas handling systems has reduced the memory to less than a few seconds, which is sufficient for resolution of chromatographic peaks (Hughey et al. 2000; Kjeldsen et al. 2008). However, there still is a long-term rise in the base line when the same cathode is used for an entire chromatogram.

At the National Ocean Sciences AMS facility (NOSAMS), we have developed a gas accepting ion source with an alternative design for continuous flow GC-AMS (Schneider et al. 2004; Roberts et al. 2007). A 2.45-GHz microwave ion source generates a plasma, which is confined in a solenoidal magnetic field. Sample CO_2 introduced with Ar carrier gas is ionized and a positive beam is extracted. The positive ion beam is passed through a Mg vapor cell where C^- ions are formed via charge transfer collisions, and then injected into the AMS system. Reasonable beam currents are produced and the ion source shows minimal short-term memory and no long-term memory.

Recently, we have developed a novel gas chromatograph-combustion system for our AMS system that allows us to flow match the GC to the AMS system and efficiently deliver micrograms of samples (of C) to the ion source (McIntyre et al. 2009). We have analyzed a variety of compounds and report herein the initial results from operation of the full continuous-flow GC-AMS system.

EXPERIMENTAL

Instrumentation. The GC, ion source, and AMS system used are described elsewhere (Roberts et al. 2007, 2010; McIntyre et al. 2009). The GC was connected to the ion source via an open split fitted with an additional capillary that could be actuated in/out of the gas stream to supply reference CO_2 at 0.38–0.40 mL/min for normalization of the sample data. The flow rate of gas from the GC (Ar + O_2) was 0.45–0.47 mL/min and into the ion source was 0.26–0.28 mL/min. Reference gas was injected in 30-s plugs periodically throughout an analytical run. This corresponded to 1.8 μmole C per plug, corrected for split ratio. The ion source was optimized for a stable ion beam at 36-kV beam energy using 100% CO_2.

Samples. Fatty acid methyl esters: A solution of fatty acid methyl esters in hexane was prepared so that 10–20 μg C per component was delivered to the ion source in a single injection (Table 1). Losses in the open split were estimated using a simple numerical model (McIntyre et al. 2009). For comparison, the fraction modern (Fm) ^{14}C values of the individual components were determined separately via conventional IRMS and AMS techniques. *Biodiesel:* The biodiesel used (B100, MA distributor A) has been described elsewhere and is known to be modern (Fm = 1.0014) (Reddy et al. 2008). It contains 3 main components that are fatty acid methyl esters of carbon number 14, 16, and 18. These are referred to as biodiesel peaks 1, 2, and 3, respectively. A solution of biodiesel in hexane was prepared with 2 internal standards that contained no ^{14}C (decane, tetracosane), and 2 that were modern (methyl dodecanoate, methyl tricosanoate). A single injection was performed such that 10–30 μg C per component was delivered to the ion source (Table 1).

Data acquisition and processing. 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 ^{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 background subtracted and normalized to the reference gas, which was known to be modern (Fm = 1.0698).

Table 1 ^{14}C analysis of fatty acids and biodiesel by GC-AMS and conventional AMS.

Sample/Component	C delivered to AMS (estimated μg)	Fm (via GC-AMS)	Error	Fm (via graphite)	Error
Fatty acid methyl esters					
Methyl decanoate (10)	15	1.04	0.09	1.028	0.004
Methyl dodecanoate (12)	12	1.03	0.11	0.993	0.004
Methyl tetradecanoate (14)	15	1.13	0.10	1.071	0.005
Methyl hexadecanoate (16)	15	0.90	0.09	1.001	0.004
Methyl heptadecanoate (17)	14	0.97	0.10	1.034	0.004
Methyl octadecanote (18)	17	0.93	0.09	1.006	0.006
Methyl nonadecanoate (19)	16	1.47	0.11	1.280	0.005
Biodiesel					
Decane	20	0.01	0.02	Fossil	—
Methyl dodecanoate	19	1.03	0.08	0.993	0.004
Biodiesel peak 1	1	0.52	0.43	Modern	—
Biodiesel peak 2	10	0.95	0.11	Modern	—
Biodiesel peak 3	25	1.06	0.06	Modern	—
Tetracosane	21	0.00	0.01	Fossil	—
Methyl tricosanoate	18	0.71	0.06	0.651	0.003

RESULTS

Traces of the ^{12}C and ^{13}C ion currents and ^{14}C counts from the analysis of the fatty acid methyl ester sample are shown in Figure 1. The ^{14}C Fm values of each component as determined by the continuous-flow GC-AMS system and conventional methods, and the estimated μg of C delivered to the ion source are given in Table 1. The peaks for individual components were 20–25 s wide with a Gaussian shape that was slightly fronted and tailed. The reference gas peaks were plug shaped and the signal decayed exponentially to background levels within 6 s with a time constant of 1 s. $^{12}C^+$ currents of up to 1 μA per component were recorded for the fatty acid methyl ester sample (s/n ~20) and up to 2 μA per component for the biodiesel sample (s/n ~40). Background signals were 0 ± 0.01–0.03 μA for ^{12}C and 2 ± 1 counts/min for ^{14}C. Precision of the Fm values ranged from 6–11% for modern peaks containing more than 10 μg C. ^{14}C counts recorded per component were 100–190 for the fatty acid methyl ester sample, 80–310 for the biodiesel sample (biodiesel peak 1 was 4 counts), and 250–350 per plug of reference gas. Overall system efficiency for conversion of the reference gas to $^{12}C^+$ was approximately 0.02% with a source efficiency of about 0.1%. In Figure 1, a spike is evident at 850 s due to an electrical breakdown in the ion source.

DISCUSSION

The purpose of this work was an initial test of the full continuous-flow GC-AMS system. The gas chromatograph-combustion system, microwave gas ion source, and compact ^{14}C AMS system were successfully coupled and we were able to perform compound-specific ^{14}C analysis at natural abundance levels for a variety of samples. For the samples analyzed here, the chromatographic peaks were well resolved and the Fm values of the individual components were consistent with those determined by conventional methods. The fatty acid methyl esters and biodiesel were modern while the petrogenic components (decane and tetracosane) were ^{14}C-dead. The fatty acid methyl ester, methyl nonadecanoate (19), was taken from a container that was approximately 30 yr old and contained elevated levels of ^{14}C derived from nuclear weapons testing.

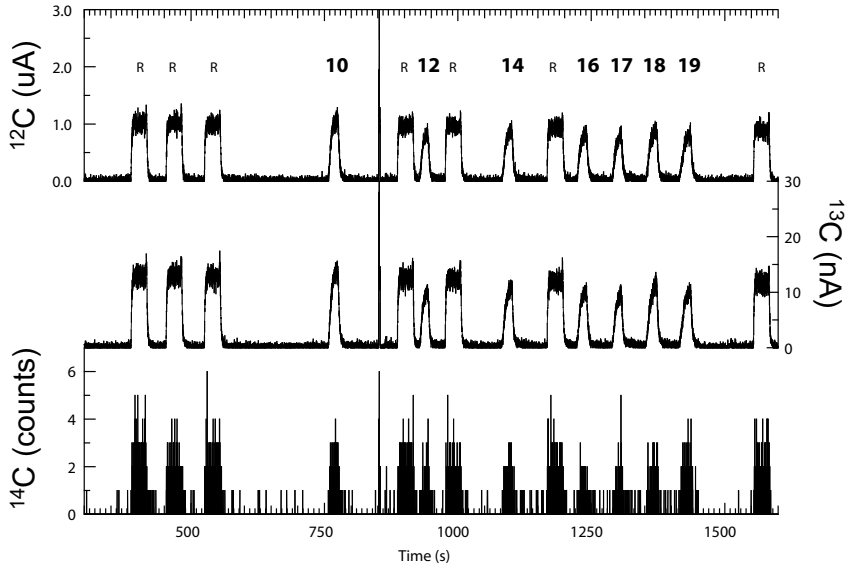

Figure 1 Compound-specific ^{14}C analysis of fatty acid methyl esters using continuous-flow gas chromatography ^{14}C accelerator mass spectrometry. Components, amount C analyzed, and Fm values are given in Table 1. Reference gas peaks are labeled with an R.

The signal for the reference gas pulse rose immediately with minimal exponential behavior, and decayed with a constant that was comparable to a hybrid source. No long-term memory occurred over the course of a run, and this was clearly an advantage of the microwave source. The lower efficiency of the source and the split ratio of 0.59 meant that a larger quantity of sample had to be injected into the GC. For these samples, we deliberately overloaded the analytical column to ensure that sufficient carbon was delivered to the ion source, so that the peaks were at least 15 s wide for data acquisition. This resulted in some chromatographic fronting and tailing of the peaks but in general, the system produced good peak shapes and resolution. The samples were reinjected several times and the results were reproducible. The response of signal to short pulses of gas and a linearity test was not investigated here.

The precision of a ^{14}C measurement is a function of the sample size and system efficiency and at natural abundance levels it is limited by counting statistics. GC-AMS systems with hybrid ion sources have an upper limit of around 1 μg C and ion source efficiencies of up to 10%, which result in a precision of ~10% per component for modern samples (Bronk Ramsey et al. 2004; Kjeldsen et al. 2008). Here, a comparable precision was obtained because, even though the ion source had a lower efficiency, it could accept a larger amount of CO_2. Only 1 component (biodiesel peak 1) was under 10 μg C, so the performance with very small-sized samples could not be accurately assessed. Whatever the case, hybrid gas ion sources retain a clear advantage here. The efficiency of the ion source for these first experiments was less than anticipated; however, continuing refinements are expected to provide further gains in this area. This would allow us to analyze smaller and older samples with greater precision and perform better chromatography. Background signals were not accurately determined here, but the signal to noise ratios (>20) were sufficient for determining ^{14}C/^{12}C ratios. These findings reinforce the point that gas ion sources (in general) are well suited to small samples, and demonstrates that our system is thoroughly competitive for CRSA.

The gas flow rate for the ion source was tested in the range 200–500 μL/min. In practical terms, this makes it easier to interface to other analytical systems. Higher flow rates mean that larger capillaries can be used in gas handling systems, and extra-column peak broadening and tailing are easier to manage. The ion source has virtually no memory and generating data is currently limited by the speed of sample introduction and length of data acquisition. The novel aspect of this system is its GC interface; however, we are also looking other interfaces such as a gas bench and elemental analyzer. These would require some form of CO_2 trapping and therefore would not be a truly real-time analysis. Theoretically, however, with a recycle time of 15 min per sample it would be reasonable to expect to be able to analyze 20–30 samples per day or more with an automated system. The gas chromatograph can readily process 8 samples a day for CSRA. With improvements to the efficiency of the ion source, the scope of the instrument will correspondingly grow.

Feasible environmental and biomedical studies at the precision level obtained in this study include reconnaissance surveys, source apportionment, and tracer studies. Reconnaissance surveys of large numbers of samples at lower precision are of interest to the oceanographic community to help understand processes at a global scale and identify individual samples for high-precision measurements. Source apportionment studies of biogenic and fossil carbon are useful for identifying fuel spills and determining biofuel composition. Tracer studies can utilize enriched compounds to track environmental processes or the fate of chemicals in humans. At enriched levels, more ^{14}C can be counted and therefore smaller sample sizes could be analyzed, a higher precision obtained and better chromatography performed.

CONCLUSIONS

The results presented here clearly demonstrate that the complete continuous-flow GC-AMS system is capable of performing compound-specific ^{14}C analysis at natural abundance levels. The gas chromatographic interface and ion source are completely novel approaches and the system represents a significant breakthrough in ^{14}C analysis. The system has better peak shape and memory than existing GC-AMS systems and a comparable precision that would make it useful for environmental and biomedical applications. Conventional hybrid sources are still more suitable for small samples. Continuing refinement of the ion source is expected to bring additional gains in efficiency, precision, and chromatographic performance. The high sample capacity and acceptance flow rate of the ion source make it compatible with a variety of analytical instruments.

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