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Installation of hybrid ion source on the 1-MV LLNL BioAMS spectrometer

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Abstract

A second ion source was recently installed onto the LLNL 1-MV AMS spectrometer, which is dedicated to the quantification of ^{14}C and ^{3}H within biochemical samples. This source is unique among the other LLNL cesium sputter ion sources in that it can ionize both gaseous and solid samples. Also, the injection beam line has been designed to directly measure $^{14}C/^{12}C$ isotope ratios without the need for electrostatic bouncing. Preliminary tests show that this source can ionize transient CO_2 gas pulses containing less than 1 ug carbon with approximately 1.5% efficiency. We demonstrate that the measured $^{14}C/^{12}C$ isotope ratio is largely unaffected by small drifts in the argon stripper gas density. We also determine that a tandem accelerating voltage of 670 kV enables the highest ^{14}C transmission through the system. Finally, we describe a series of performance tests using solid graphite targets spanning nearly 3 orders in magnitude dynamic range and compare the results to our other ion source.

Keywords: AMS, ion sources, CO_2 gas, graphite

Introduction

The 1-MV spectrometer at the Center for Accelerator Mass Spectrometry, located at Lawrence Livermore National Laboratory, is dedicated to the quantification of ^{14}C[1] and, recently, ^{3}H[2] within biochemical samples. Over 50,000 samples have been analyzed since operations began in May 2001. High measurement throughput is enabled by the use of the LLNL high-output Cs-sputter solid sample ion source[3].

The use of solid targets necessitates the off-line conversion of biochemical samples to graphite[4] or TiH_2[5]. Ion sources that are compatible with the direct input of biochemical separatory instrumentation, such as liquid chromatography, gas chromatography, capillary electrophoresis or other instruments would allow for real-time, automated sample preparation, potentially leading to increased resolution, improved sensitivity through reduced sample handling and the ability to do molecule-specific tracing of very small samples, but with a cost in precision. One such approach would involve the direct introduction of carbon, as CO_2, into the ion source. As the LLNL-designed ion source will only accept solid samples, a gas-accepting ion source was installed. This source is a heavily-modified version of the NEC MCGSNICS ion source and is designed to accept both solid and gaseous samples [6].

The injection beam line of this ion source has been designed to allow for the simultaneous measurement of $^{14}C^{+}$ and $^{12}C^{-}$ ions without the need for electrostatic isotope switching. In this case, the $^{12}C^{-}$ ions are measured in an off-axis Faraday cup after a magnet located immediately after the ion source. High accuracy and precision require that the transmission of the ^{14}C ions through the entire beam line remain constant. In our system, the largest source of transmission variations is from changes in the stripper gas density, which can drift 5-8% during the course of a day's operation. We measured the extent of this effect, as well as changes in the tandem accelerating voltage on ^{14}C ion transmission.

In order to have confidence in the results obtained using this new ion source, a series of performance tests were conducted using solid graphitic targets with $^{14}C/C$ isotope ratios spanning

3 orders in dynamic range, which encompasses the majority of bioAMS samples. The use of solid graphitic targets allowed for the direct comparison of the performance of this source to that of the other ion source which can only accept solid samples.

Description

Figure 1 is a schematic layout of the 1-MV AMS system. The new ion source and its associated injection beam line is attached through an existing port of a 45° electrostatic analyzer which can rotate to enable the operation of either ion source. The new injection beam line has been designed to allow for the direct quantification of either $^{14}C/^{12}C$ or $^{3}H/^{1}H$ isotopic ratios [7; 8; 9; 10]. This configuration increases our ^{3}H-AMS measurement throughput as it eliminates slow magnetic field switching of the injector magnet that is required when using our other source.

As purchased from National Electrostatics Corporation (Middleton, WI), the MCGSNICS ion source required significant modifications to improve its output and to provide easier access for maintenance. Many of these modifications were based on the work of Southon et al. [8; 9; 10]. Additionally, for ease of servicing and replacement, we wanted to use the same spherical ionizer and cesium delivery shroud design that is used on the other LLNL-designed ion sources. This ionizer replaced the NEC-supplied conical ionizer. Other modifications included the installation of an immersion lens to replace the cesium focus lens, a large aperture extractor, and a large inner diameter insulator to replace NEC components. We also opened up the interior to provide for better vacuum pumping. Table I outlines typical operating parameters.

Preliminary Gas Sample Performance

Key to the performance of this source is its gas ionization capabilities. In particular, we are interested in the measurement of a transient CO_2 pulse generated by an online combustion interface which is directly coupled to biochemical separatory instrumentation, such as high

performance liquid chromatography (HPLC). Rapid response with minimal tailing coupled with a high ionization efficiency will ensure that the peak resolution obtained from the HPLC is maintained. To that end, we designed a gas target that fits within the constraints of the NEC sample changer and directs the flow of the CO_2 through the target and maximizes its contact with the incoming cesium ion sputter beam [11].

Using our moving wire combustion interface [12], we generated CO_2 pulses from 2 ul drops of an aqueous sucrose solution each containing approximately 600 ng carbon. The CO_2 pulse was transported in helium gas stream along a 6 m long x 150 um i.d. fused silica capillary to the gas ion source. Total gas flow was estimated to be 0.35 sccm. Figure 2 shows a plot of the recorded $^{14}C^{+}$ count rate and $^{12}C^{-}$ ion current of four of the 23 peaks recorded over a 30-minute period. The peaks all exhibited a rapid rise time of approximately 5 seconds from baseline to peak, followed by a slower return to baseline. Average peak widths were 7.5 seconds, which is on par with the calculated 8-second sweep time of the gas through the combustion oven of our moving wire interface. We calculated an average ion source efficiency of 1.5%, assuming the efficiency of the interface is 100%. The isotope ratio was determined by manually selecting the limits of the peak based on the $^{12}C^{-}$ data and subtracting an appropriate background as determined by the data immediately preceding each peak. The average and 1 sigma standard deviation of the isotope ratio was calculated to be 2.91±0.23 counts ^{14}C/uCoul ^{12}C. The 8% precision about the average value is close to the 7% precision expected from pure counting statistics of the roughly 200 ^{14}C counts contained in each peak.

Stripper Dependence on Ratio

Our 1-MV AMS spectrometer uses a diffuse argon gas in a recirculating stripper canal to break up interfering molecular isobars. The gas density is monitored with a thermocouple gauge located above the stripper canal and a gas pressure of at least 42 mTorr is required for complete molecular ion destruction. However, ion losses due to scattering increases as gas density

increases. This ion source measures the stable isotope prior to entering the accelerator so any drift in the stripper pressure will result in a change in the measured isotope ratio. We wanted to investigate the magnitude of this effect.

Figure 3 shows the results of 10-second measurements of a graphitic sample of ANU sucrose while varying the stripper pressure. At stripper pressures below 40 mTorr, incomplete molecular isobar destruction is evident while the isotope ratio slowly decreases at stripper pressures above 40 mTorr, which is a direct result of ^{14}C ion losses due to scattering. The inset plot shows the data around our normal operating pressure range from 42 to 48 mTorr. In this region, the isotope ratio varies by 3%, which is approximately equal to the variation expected from the counting statistics derived from the ~1000 ^{14}C counts in each data point.

This indicates that for biomedical AMS measurements, the effect of stripper pressure on the measured ratio can be ignored as long as the stripper pressure is not allowed to drift outside of the 42-48 mTorr normal operating pressure.

Transmission

The optimal transmission through the stripper canal depends on the careful matching of the accelerator entrance lens with the injected ions' energy and mass. Again, since our system measures the $^{12}C^-$ ions after the switching magnet and we do not bounce the ions through the accelerator, we wanted to select the optimal tandem accelerating voltage to maximize the ^{14}C transmission. Maximizing the ^{14}C transmission has a direct impact on the precision that can be obtained from a transient CO_2 peak injected into the ion source from a continuous flow interface.

We measured the $^{14}C/^{12}C$ ratio for a graphitized ANU sucrose sample while varying the tandem accelerating voltage. We tuned the high-energy end of the system at each energy and then measured the ANU sucrose sample for 30,000 ^{14}C counts. The transmission was calculated by

comparing the measured ratio to the expected ratio of the ANU sucrose, which has an accepted $^{14}C/C$ ratio of 1.508 Modern.

The results are plotted in Figure 4. The ^{14}C ion transmission reaches a narrow plateau of ~35% at tandem energies between 660 kV and 680 kV. Ion losses can arise from at least three main sources: losses due to scattering, losses due to charge state distribution and, to a lesser extent, losses due to molecular ion formation in the ion source (i.e., $^{14}CH^-$). No attempt was made to differentiate between these three sources, although nearly 50% of the ions should be in the +1 charge state at this energy [13]. Instead we focused on empirically determining the optimal tandem accelerating voltage that would give the highest transmission for the ^{14}C ions.

Solid Sample Reproducibility and Comparison

As a comparison to results obtained from our standard ion source, we prepared [4] and measured solid graphitic samples of material whose $^{14}C/C$ content ranged from 0.1 Modern to 100 Modern. These levels of ^{14}C span the vast majority of concentrations found in bioAMS samples. Each samples was measured 4-7 times with the collection of at least 10,000 ^{14}C counts or for 30 seconds, whichever came first. The data were taken over 5 days within a 2-week period. Raw ratios were normalized to similarly prepared and measured samples of ANU sucrose.

The data is summarized in Table II by showing the averages of all the samples. Also, we compare our results to that obtained using our standard ion source. The data compares favorably except for the 0.1 Modern tributyrin sample. These samples are at the lowest level of our typical bioAMS samples and are not measured to as high a precision as the other sample types. Typical throughput using this ion source was ~95 samples/day.

Conclusions

These results from our newly installed ion source demonstrate its effectiveness in reliably measuring $^{14}C/^{12}C$ isotope ratios from solid graphite targets. However, much work remains to be completed before the source and interface are brought into service for routine analysis of transient CO_2 pulses. In particular, the effects of sample-to-sample cross contamination on ion source and interface operation need to be fully understood. Before we can begin tests with CO_2 containing elevated levels of ^{14}C, we must demonstrate that we are preventing the release of $^{14}CO_2$ into the room atmosphere. While these amounts do not present a health hazard, they do represent a potential source of contamination that could negatively impact the ultrasensitive, low background ^{14}C-AMS measurements that are conducted on our 10MV FN tandem, which is co-located in the same building.

Acknowledgements

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Figure Captions

Figure 1. Schematic layout of the 1-MV AMS system showing the newly installed hybrid source. The main elements are listed as follows: (1) hybrid source, (2) 45° switch magnet, (3) $^{12}C^-$ Faraday cup, (4) 45° electrostatic analyzer with rotatable field plates, (5) 1 MV tandem accelerator, (6) $^{14}C^+$ and $^3H^+$ detector, and (7) LLNL solid sample ion source.

Figure 2. Measured $^{14}C/^{12}C$ ratios of CO_2 pulses prepared from 2 ul drops of an aqueous sucrose solution each containing approximately 600 ng carbon. The black line represents the measured $^{12}C^-$ ion current while the gray line is the measured $^{14}C^+$ counts.

Figure 3. Plot of measured $^{14}C/^{12}C$ ratio of a graphitized ANU sucrose sample with respect to argon gas pressure in the molecular dissociation cell of the 1-MV tandem accelerator. The inset shows a detail of the data between 40-50 mTorr. The increase in the $^{14}C/^{12}C$ ratio at pressures below 40 mTorr is caused by incomplete molecular ion dissociation. At pressures above 40 mTorr, increased ion scattering results in the decrease in the $^{14}C/^{12}C$ ratio.

Figure 4. Plot of ^{14}C ion transmission with respect to tandem energy. See text for details.

Table I. Hybrid ion source operating parameters and typical performance

Source Operating Parameters		Source Performance	
Cathode Voltage	9 kV	Operating Pressure	6 x 10^{-7} Torr
Extractor Voltage	12 kV	Ion Energy	49 keV
Bias Voltage	40 kV	Ion Current	125 uA $^{12}C^-$ (graphite)
Cesium Temperature	170 °C	$^{14}C/C$ Background	~10^{-14} (gas) 2x10^{-15} (graphite)
Ionizer Power	135 W		

Table II. Summary results of measured $^{14}C/C$ isotope ratios for samples ranging between 0.1 and 100 Modern. Average values of similar samples as measured on the LLNL ion source are also presented.

	Hybrid Source	LLNL Source
Sample	FM Average	
0.1 Modern Tributyrin	0.1004 ± 0.0081 (8.1%)	0.1195 ± 0.0119 (10%)
0.25 Modern Tributyrin	0.2331 ± 0.0079 (3.4%)	0.2728 ± 0.0100 (3.7%)
ANU Sucrose (1.5 Modern)	1.509 ± 0.019 (1.3%)	1.508 ± 0.0010 (0.7%)
12 Modern Oxalic Acid	12.20 ± 0.36 (3.0%)	12.32 ± 0.21 (1.7%)
100 Modern Oxalic Acid	104.4 ± 2.7 (2.6%)	102.2 ± 1.7 (1.7%)

Figure 1

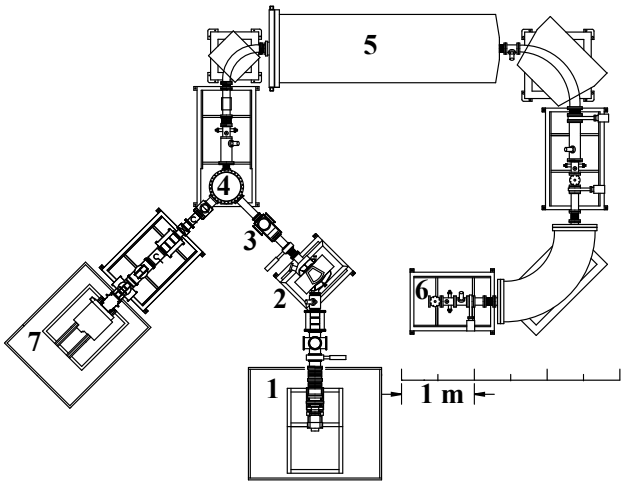


Figure 2

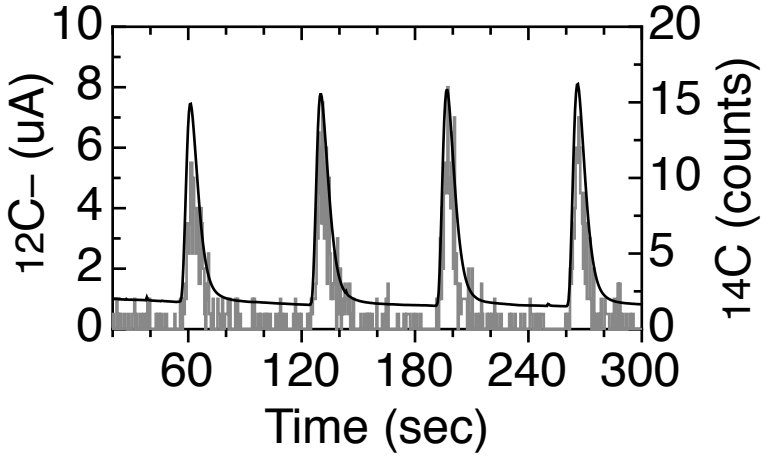

10
8
6
4
2
0
$^{12}C^-$ (uA)
20
15
10
5
0
^{14}C (counts)
60
120
180
240
300
Time (sec)

Figure 3.

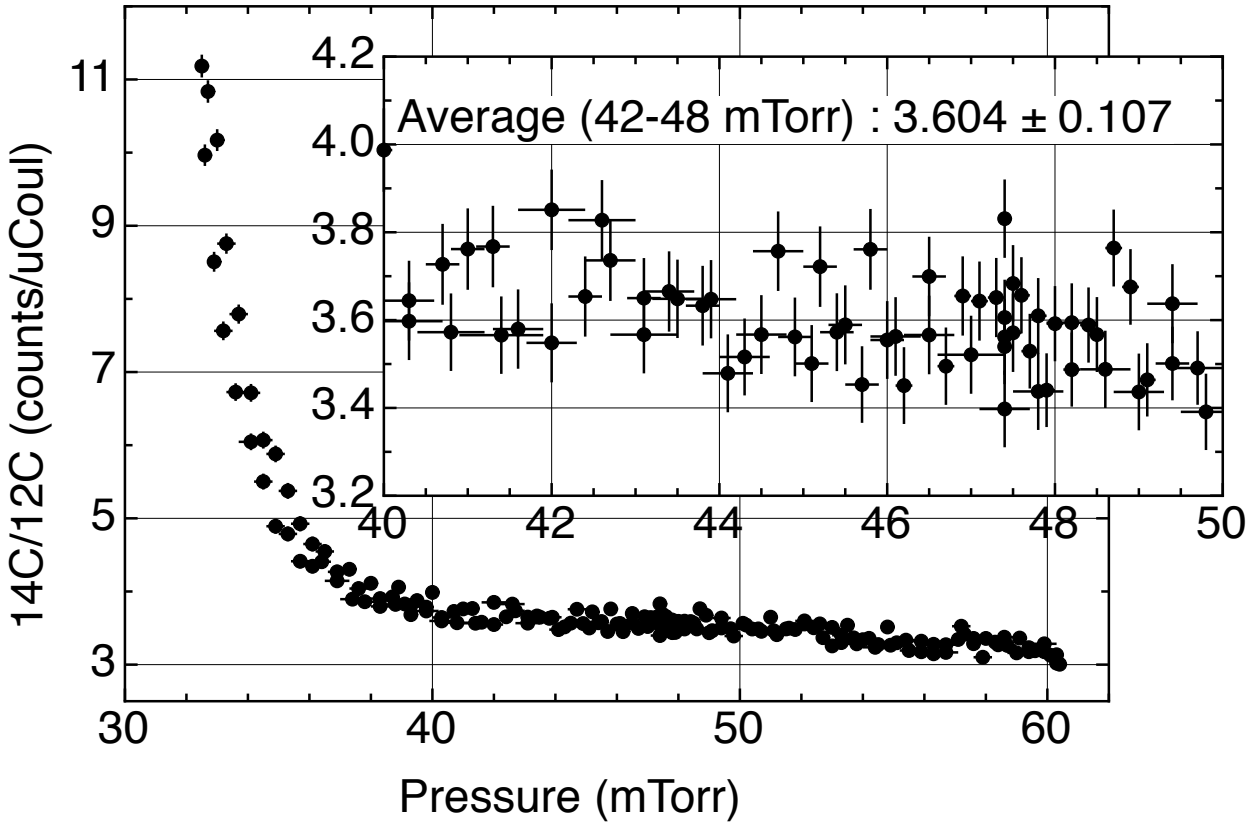
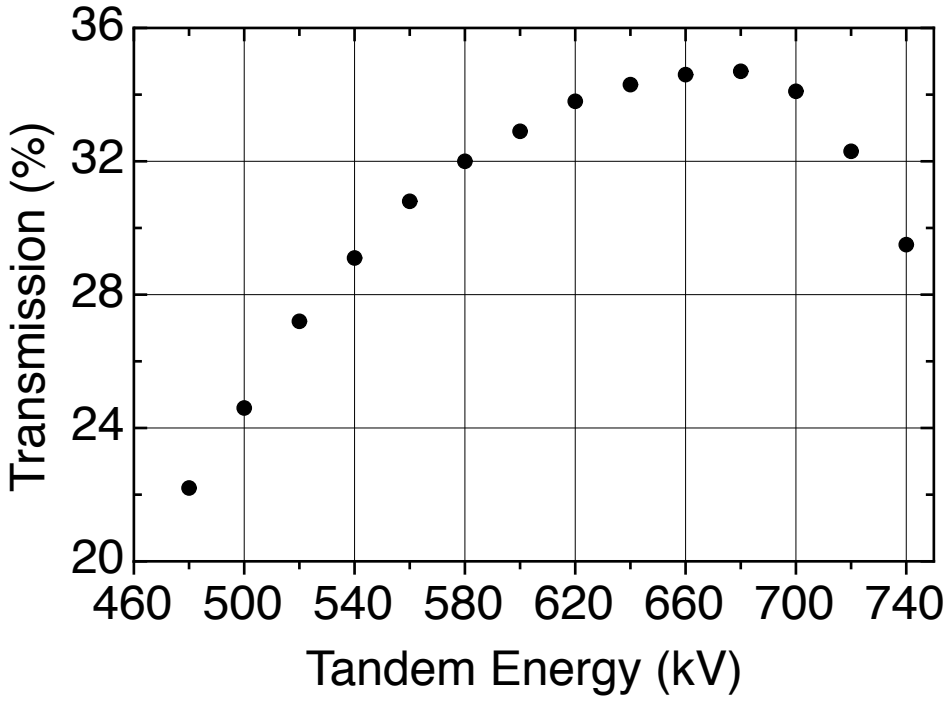

Average (42-48 mTorr) : 3.604 ± 0.107
14C/12C (counts/uCoul)
Pressure (mTorr)
11
9
7
5
3
30
40
50
60
4.2
4.0
3.8
3.6
3.4
3.2
40
42
44
46
48
50

Figure 4


Transmission (%)
36
32
28
24
20
460
500
540
580
620
660
700
740
Tandem Energy (kV)