A gas ion source for continuous-flow AMS

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Abstract

The first gas-fed ion source for radiocarbon AMS applications (without sputtering) has been operated at the Woods Hole NOSAMS Facility. A three-year, off-line test program resulted in positive carbon ion currents up to 1 mA and negative ion currents up to 80 μA. Recently, the compact, permanent-magnet microwave plasma ion source and magnesium vapor charge-exchange canal were coupled to the recombinator injector of the 2.5 MV Tandetron. When the ion source was operated on CO_2 at a flow rate of about 200 μl per minute, negative carbon ion beams up to 20 μA were obtained, at an energy of 35 keV. Radiocarbon measurements were performed on standard reference gases and the dynamic response to square-wave pulses of gas was determined. Time constants in the ion source are less than 1 s, which should allow analysis of chromatographic peaks of CO_2 with very little broadening. A combustion device has been constructed to generate CO_2 for direct injection into the source. Argon carrier gas is used to buffer the pressure at one atmosphere in the sample gas injector. A dedicated ion-beam injector, with higher angular acceptance and higher transmitted currents, is being constructed for the AMS system.
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1. Introduction

A microwave plasma ion source has been tested extensively using a test stand which included a silica-capillary-based gas handling system to produce constant flows in the range of 100–1000 μl/min into a plasma discharge. When a flow of CO_2 was introduced into the ion source, a positive ion current was extracted and analyzed with a spectrometer magnet. Small samples containing several micromoles of CO_2 could be entrained in a stream of argon used as a carrier gas. In this way, a stable plasma discharge was maintained. To obtain negative carbon ions for use in AMS systems, a charge-exchange canal was inserted immediately following the ion source. The argon beam was largely neutralized and passed into a beam dump whereas the negative carbon ion beam was analyzed. The results of these tests have been reported in [1–3]. A short summary appears in Table 1. The efficiency of producing positively charged carbon

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Table 1

Typical microwave ion source test stand results, with a 5-mm extraction aperture and a 5-mm gap and gas flows of 0.25 ml/min

Analyzed current	Extraction supply	Canal temperature (°C)	RF power (W)
2.5 mA, argon	35 kV/12 mA	50	84
735 μA, $^{12}C^+$	35 kV/15 mA	50	220
81 μA, $^{12}C^-$	35 kV/15 mA	498	221

ions from continuously flowing CO_2 molecules with this ion source is about 4% and the conversion yield of the charge exchange process is about 8.5%.

We obtained positive carbon ion currents close to 1 mA and measured $^{13}C/^{12}C$ ratios with instability of less than 1% over a 20 h period. We began by using pure CO_2 gas flowing into the ion source at about 0.2 ml/min. We also constructed a gas-pulse injector (described in [1], with the latest version shown in Fig. 1) for studying the time-response of the system to well-defined pulses of CO_2 carried within an argon carrier gas stream. With this device, we learned the importance of eliminating small dead volumes of gas, which can contribute to long tails on injected gas pulses and consequently on the ion pulses. The efficiency of C^+ ion production in pulse mode is reduced from
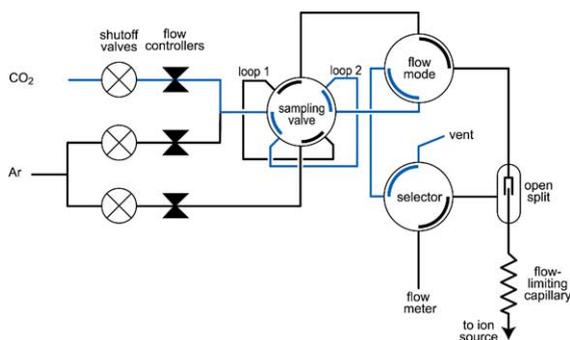

Fig. 1. Gas-sampling system used in testing and development of the microwave ion source. Each of the large circles represents a valve in which alternate sets of adjacent ports can be connected. In the state shown, loop 1 is being purged with Ar carrier gas which is flowing to the open split. The gas not being accepted by the flow-limiting capillary is being directed to a flow meter. Simultaneously, loop 2 is being filled with CO_2. Toggling the sampling valve places the CO_2 sample into the stream being sent to the ion source.

the continuous flow mode, by the splitting factor of the open split (as shown in Fig. 7).

There are generally two components in the decay of an ion pulse from the source. The short component, with a time constant less than 1 s, depends on ion extraction from the plasma discharge. The long component, with a time constant 10–100 s or more, is dominated by the release of molecules from these trapped volumes but also includes delayed release of molecules which stick to the walls of the discharge chamber. We believe that the AMS community has been discouraged in the past from pursuing this method in the mistaken belief that it was the wall effect which dominated the tailing rather than simple, dead-volume trapping. At the Lawrence Berkeley Laboratory, where radioactive beams are generated with high frequency ECR (Electron Cyclotron Resonance) ion sources, the decay times for $^{11}C^{4+}$ have been measured [5]. The fast component was 3 to 6 s, and the slow component was about 6 min. The latter was thought to represent wall-sticking from the plasma chamber, but may have also been influenced by small trapped volumes.

Since we needed to produce negative ions for injection into the tandem accelerator, we then added a magnesium vapor charge exchange canal and were able to obtain negative carbon ion currents up to 80 μA. In the past, sodium, lithium and cesium have all been used as donors of electrons for negative ion formation. A comprehensive study was made at University of Aarhus in the late 1970s [4]. The equilibrium charge state fraction for carbon ions (having an electron affinity 1.268 eV) in magnesium vapor was around 10%. There is both less scattering and a lower equilibrium target thickness for carbon ions in magnesium vapor than in the heavier alkali vapors. As a practical matter, the handling and cleaning of sodium- and lithium-vapor charge-exchange canals has often

reduced the efficiency of use. The magnesium sublimes directly from a solid to a vapor. No dangerous condensates are formed and the scale on the copper heat-shield can be soaked off in a bucket of water (outdoors, for release of hydrogen). The 1 cm diameter by 16 cm long vapor cell [3] is operated at a temperature of 495 °C. The beam emerging from the canal has a half-angle of 0.71°. We obtain about 8.5% efficiency for the production of negative carbon ions.

2. Installation on the AMS

In December of 2001 we mounted the microwave ion source and charge-exchange canal onto the recombinator injector of the NOSAMS accelerator for a test. To do this, it was necessary to temporarily dismount the NEC-MCSNICS sputter ion source from one of the recombinators. The arrangement is shown in Fig. 2. The acceptance of the recombinator is limited, so we inserted a water-cooled, 5-mm aperture to limit the beam emerging from the charge-exchange canal to a half-angle of 0.25°. The resulting intensity was about 23% of the total output. We also installed graphite blocks in the first magnet chamber where we expected argon ions to hit if they were not neutralized by the

charge-exchange canal. Tests were carried out from January to early May, 2002, during intervals in the radiocarbon-analysis production schedule. At first, pure CO_2 was introduced into the ion source. Ions were extracted at 35 kV, with the
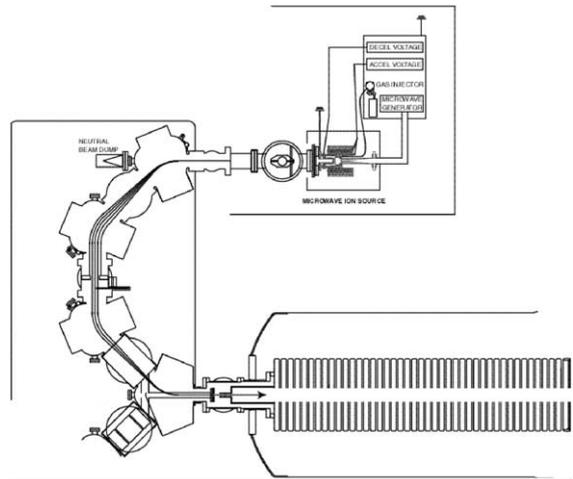

Fig. 2. Plan view of the microwave ion source and charge-exchange canal as they were installed on the recombinator injector of the AMS system, January 2002. A neutral beam dump, consisting of a water-cooled copper cylinder, was used to collect the Ar beam from the Ar carrier gas. Not shown is the other injector, or the complete accelerator.
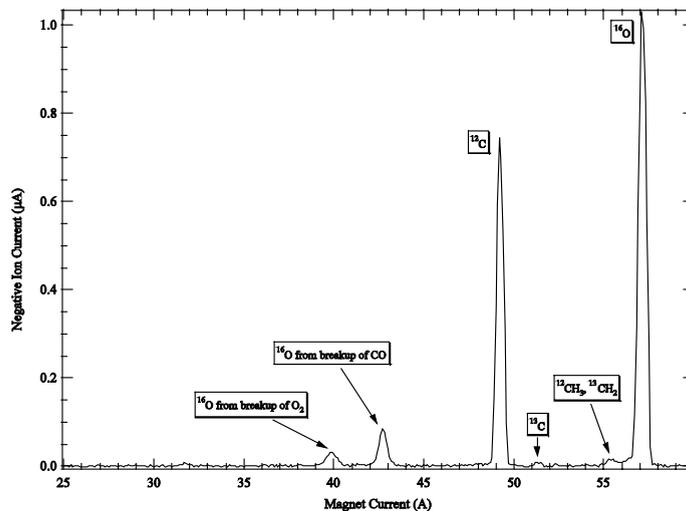

Fig. 3. Mass spectrum as measured with a Faraday cup in the symmetry plane of the recombinator. There appears to be very little hydride component present, as the gas was pure CO_2.
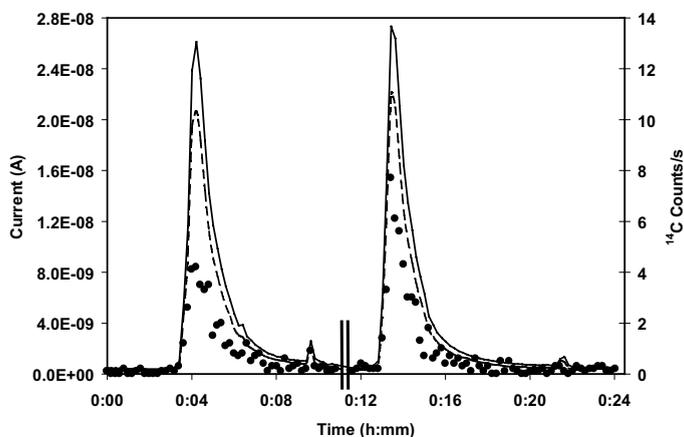
Fig. 4. Currents of ^{12}C (solid lines) and ^{13}C (dashed lines) and counts of ^{14}C as collected from combusted HOxI (left) and HOxII (right) samples. The numbers of counts collected were 421 and 510, respectively. The ^{12}C current is attenuated by a rotary chopper to about 1% of its full intensity.
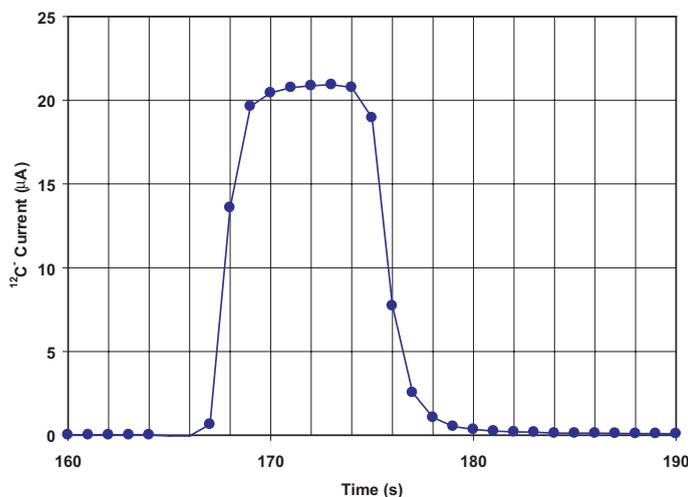

Fig. 5. A carbon current pulse as measured by the AMS system, representing a 1.1 μmol CO_2 sample injected over 10 s utilizing the system shown in Fig. 1. The fast decay has a time constant less than 1 s.

suppression electrode at −1.8 kV to minimize back-streaming electrons. A mass spectrum was obtained from the Faraday cup in the symmetry plane of the recombinator. It is shown in Fig. 3. One of the first things noticed was the absence of significant hydrides, compared with output of the sputter ion source. (This may be related to the use of small amounts of hydrogen in the preparation of graphite.)

For the attempt to detect radiocarbon, we required a convenient source of modern CO_2 since tank CO_2 is radiocarbon dead. Accordingly, the first ^{14}C/^{12}C ratios were measured on CO_2 gas collected from fermenting beer and also from combusted oxalic acid standards and dead graphite blanks. We obtained a fraction modern of 1.068 for the beer gas, consistent with a modern taste! Data were acquired for the three carbon isotopes

simultaneously, as is done with the sputter ion source, with ten-second integration times. Fig. 4 shows the counts collected from combusted HOxI and HOxII samples. A 2-m length of 100 µm capillary was used to limit the gas flow rate to 0.25 ml/min. The overall efficiency for detection of ions by the AMS system was equivalent to 0.001 ions at the collector per molecule of continuously flowing gas introduced to the ion source. For pulse-mode operation, the samples were loaded into 108 µl sample loops, for injection into the carrier. The AMS system response to a single 1.1 µmol pulse is shown in Fig. 5. The integration time was one second for this data. An examination of the falling side of the pulse reveals the fast (0.87 s) and slow (13.0 s) components. This has encouraged us to think of possible applications to chromatography, where the slowly varying outputs could easily be resolved by this gas ion source system. The maximum ^{12}C current we were able to obtain in the recombinator during these tests was 20 µA due to the limited acceptance. System background counts were as low as those observed with the sputter ion source except during transmission of intense argon beams through the first magnet. Further investigation of scattered beam events needs to be done.

3. Conclusions and future plans

To work around the limited acceptance of the recombinator, we are currently building a new injector which will be installed on the axis of the accelerator, as shown in Fig. 6. This will permit us to utilize the full output of the microwave ion source by using the accelerator solely as a ^{14}C detector, with the negative ^{12}C beam being measured off-axis in the injector. The charge-exchange canal is being closely coupled to the ion source, for optimum transmission. Here we will rely on the stability of the AMS system over measurement cycles of at least one hour, which has been adequately demonstrated. Major components of the injector include a new double-focussing spectrometer magnet with 70-mm aperture (Buckley Systems, Auckland, New Zealand), dual Faraday cups to collect ^{12}C and ^{13}C, and an einzel lens to focus the ^{14}C beam into the accelerator. We will operate this injector off-line initially and install it on the accelerator during 2003. During this period, we will further investigate combustion devices for producing and drying CO_2.

Applications will be quite different from those using the sputter ion source. Continuously varying radiocarbon sources can be measured rather than static samples. A different class of sample materials should be anticipated, since the efficiency (carbon ions per CO_2 molecule) is about 1/10 that of the best sputter source. Also, the ideal flow rate for the present ion source is about 1/10 that of a standard GC instrument. Methods of separating and splitting sample and carrier gases will have to be developed. Precision expected for $^{14}C/^{12}C$ with these limitations is shown in Fig. 7. Such a system would lend itself to detection of the absence of radiocarbon in otherwise super-modern materials,
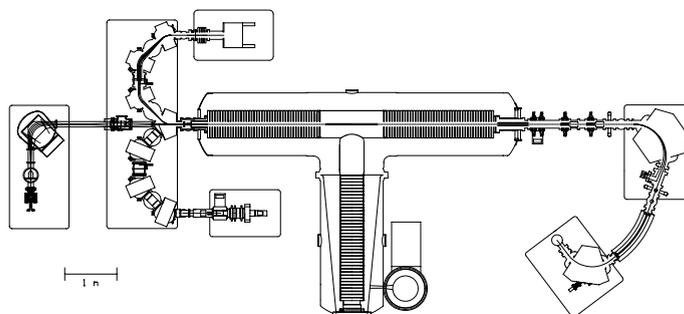

Fig. 6. Plan view of the future installation of a gas ion source injector on the AMS system. The injector is at the extreme left. Not shown is the neutral beam dump after the magnet. A lens and steerers will be used to introduce the beam into the zero-degree port of the accelerator. The (negatively charged) stable isotopes will be measured after the magnet, and only the radiocarbon will be counted by the AMS.
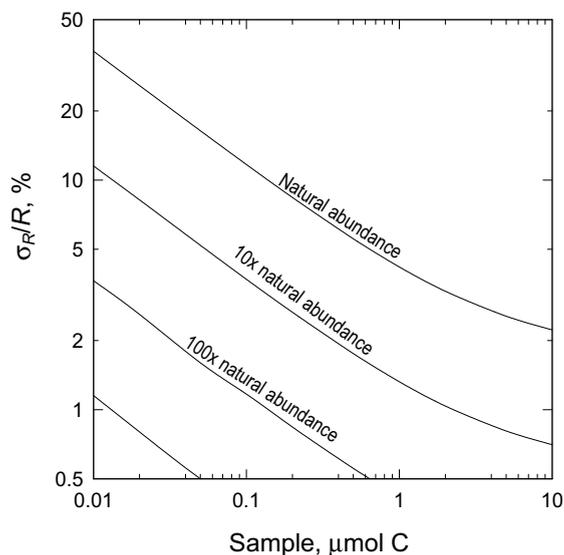
Fig. 7. Precision of $^{14}C/^{12}C$ ratio measurements as a function of sample size and ^{14}C abundance for continuous-flow analyses in which a 20 s wide pulse of CO_2 is added to argon carrier gas flowing at 0.25 ml/min. The ion source is assumed to accept 0.2 ml/min. The split efficiency is thus 80% for small samples but lower for large samples, in which the CO_2 may raise the flow rate, leading to the non-linearity observed.

in other words as an inverse tracer. The profiling of layers in sediments with an embedded oil spill, or the measurement of a gas which is continuously evolving from a chemical or biological reactor, come to mind. A simulated chromatogram containing components ranging from radiocarbon dead to 2× modern has been developed in order to explore the expected performance of the system.

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