CONTINUOUS-FLOW ACCELERATOR MASS SPECTROMETRY FOR RADIOCARBON ANALYSIS

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Continuous-Flow Accelerator Mass Spectrometry for Radiocarbon Analysis

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Abstract

Accelerator Mass Spectrometry (AMS) is a widely used technique for radiocarbon dating of archaeological or environmental samples that are very small or very old (up to 50,000 years before present). Because of the method's extreme sensitivity, AMS can also serve as an environmental tracer and supplements conventional nuclear counting techniques for monitoring ^{14}C emissions from operating nuclear power plants and waste repositories.

The utility of present AMS systems is limited by the complex sample preparation process required. Carbon from combusted artefacts must be incorporated into a solid metallic target from which a negative ion beam is produced and accelerated to MeV energies by an accelerator for subsequent analysis. This paper will describe a novel technique being developed by the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Laboratory at the Woods Hole Oceanographic Institution for the production of negative carbon ion beams directly from a continuously flowing sample gas stream, eliminating the requirement for a solid target. A key component of the new technique is a microwave-driven, gaseous-feed ion source originally developed at Chalk River Laboratories for the very different requirements of a high current proton linear accelerator. A version of this ion source is now being adapted to serve as an injector for a dedicated AMS accelerator facility at NOSAMS.

The paper begins with a review of the fundamentals of radiocarbon dating. Experiments carried out at NOSAMS with a prototype of the microwave ion source are described, including measurements of sample utilization efficiency and sample "memory" effect. A new version of the microwave ion source, optimized for AMS, is also described. The report concludes with some predictions of new research opportunities that will become accessible to the technique of continuous-flow AMS.

Key Words: Environmental Science, Radiocarbon Dating, Accelerator Applications.

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INTRODUCTION: NOSAMS

This paper describes a collaborative effort between the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) of the Woods Hole Oceanographic Institution (WHOI) and Chalk River Laboratories (CRL) to develop a new Accelerator Mass Spectrometry (AMS) system designed specifically for continuously monitoring ^{14}C in a flowing gas stream. The instrument will be capable of continuously analysing chromatographic effluents and determining the abundance of ^{14}C in individual chromatographic peaks.

An essential component of the new AMS system will be an ion source specifically designed to accept gaseous feeds and optimised for the injection of carbon ion beams into the new accelerator. An ion source possessing many of these characteristics has been under development at CRL, for a completely different application.

This paper presents a brief review of radiocarbon dating and accelerator mass spectrometry. The development of the ion source at CRL is described, in the context of AECL research into high-power, high duty factor accelerator structures. Some examples of experiments at NOSAMS that established the compatibility of the Chalk River ion source with the requirements for "continuous flow" AMS are summarised and the design of a new ion source based on this experience is described. The paper concludes with some speculative thoughts about the new fields of research that will be made accessible by the continuous flow AMS facility.

RADIOCARBON DATING

Carbon 12 (^{12}C), ^{13}C and ^{14}C are the most common isotopes of carbon present in nature. ^{12}C and ^{13}C are stable, with abundances of about 99% and 1% respectively. The natural abundance of ^{14}C is about 1 part in 10^{12} relative to ^{12}C. ^{14}C is produced at a nearly constant rate by the interaction of cosmic ray neutrons with nitrogen atoms in the upper atmosphere. The ^{14}C formed is rapidly oxidized to $^{14}CO_2$ and enters the earth's plant and animal lifeways through photosynthesis and the food chain. ^{14}C also enters the Earth's oceans in an atmospheric exchange and as dissolved carbonate.

^{14}C is unstable, with a half-life of 5730 years. Since this rate is slow relative to the movement of carbon through food chains (from plants to animals to bacteria) all carbon in biomass at earth's surface contains atmospheric levels of ^{14}C. However, as soon as any carbon drops out of the cycle of biological processes - for example, through burial in mud or soil - the abundance of ^{14}C begins to decline through radioactive decay. This process is the basis of carbon dating.

One method for determining the radiocarbon age of a sample is by the β-counting technique developed originally by Libby in the late 1940s [1]. ^{14}C decays to ^{14}N by beta emission with an average beta energy of 50 keV. A 1-gram sample of "modern" carbon produces approximately 14-beta counts/minute. To measure the age of a relatively modern sample to ±20 years would require 1.6×10^5 counts or 8 days. In some cases, one can increase the mass of the sample to obtain a more reasonable measurement, but this is not always possible. Fortunately, a much more sensitive dating method is now available.

1. Accelerator Mass Spectrometry

Accelerator Mass Spectrometry [2, 3] allows the dating of milligram samples of carbon. This technique was developed during the 1970s and has undergone continuous improvement and elaboration to the present. Dedicated accelerator systems are now available commercially to carbon date a wide variety of sample types on an automated basis. A typical conventional AMS system is shown schematically in Figure 1.

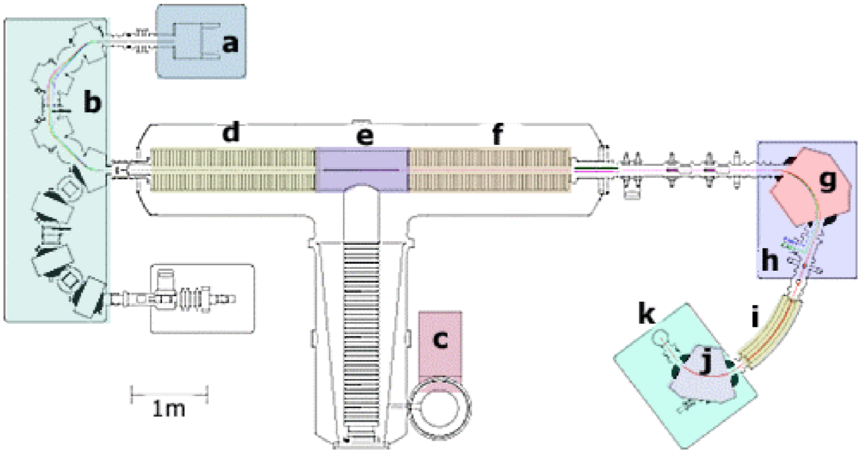

Figure 1: Schematic of AMS Facility

Before analysis by the AMS system, the sample requires considerable processing to render it into a form acceptable to the accelerator. Samples are combusted to produce CO_2, which is then converted to graphite at high temperature. The graphite is pressed into a pellet, which is inserted into the sputter target of an ion source (location a, Figure 1). The graphite pellet is bombarded by a beam of Cs ions, which sputter ionized atoms of carbon from the surface of the pellet. The ions created by this process are negative ions (that is, an extra electron is attached instead of removed, giving the atom a net negative charge of –1). This is crucial for carbon dating because it is necessary to discriminate against the abundant natural isotope ^{14}N, which does not form a stable negative ion. The ions are extracted from the ion source by biased electrodes and formed into a beam for further acceleration and analysis in the accelerator. The entire process of beam formation and acceleration takes place in hard vacuum.

The ion beam then passes through a series of magnetic and electrostatic lenses (known as the recombinator), b, where the beam is separated by mass and the components outside the mass range of the carbon isotopes of interest (mass 12 – 14) are rejected. The purified beam is then accelerated towards the terminal of a tandem Van de Graaf accelerator (e), which is maintained at a potential of 2.5 million volts (MV).

The terminal contains an electron stripper canal (e), a tube of about 1.25 cm diameter containing a small amount of argon gas. As the negative ion beam passes through the stripper canal, up to half of the ions are "stripped" of four of their valence electrons. The now-positive ion beam experiences a repulsion from the terminal (hence, tandem accelerator).

The main mass spectrometer magnet (g) bends the (3+) carbon ions through 110°, separating the three isotope beams by mass. Two faraday cups at (h) measure the ^{12}C and ^{13}C currents. The ^{14}C beam passes on through a 33° electrostatic filter (i) and a 90° bending magnet (j) for further filtering, to a sensitive gas counter (k). The raw data for the measurement is generated by a comparison of the count rate of ^{14}C in the detector and the ^{12}C and ^{13}C currents measured at the faraday cups. The radiocarbon age of the sample is therefore determined by a direct determination of the amount of ^{14}C in the sample, instead of counting the decay of the isotope.

The measured samples are routinely compared to “background” samples made from materials that are radiocarbon “dead”. The limit of detection for most AMS laboratories, determined from the background measured from dead samples, is typically of the order of 55,000 years before present.

SAMPLE PROCESSING

The amount of graphite needed to fabricate a sputter target in a conventional AMS system is approximately 1 mg. If sufficient sample material is available, precision in dating of the order of 0.4% is obtained. However, for samples smaller than 50 µg, it is difficult to prepare graphitic targets that produce a stable ion beam. The team at NOSAMS have prepared stable targets with amounts as low as 20 µg by multiple chromatographic runs with trapping of effluent fractions and recovery of the fractions, but the technique could benefit from improvement and simplification. This could be accomplished by abandoning the stepwise processing involved in producing a sputter target for an “on-line” system in which analytes flow directly and continuously from a gas chromatograph into the ion source. An on-line system would also tend to reduce the risk of introducing errors from contamination by environmental carbon, by reducing the number of processing steps the sample is subjected to.

An on-line system could be realized by adopting an ion source, which is designed from the outset to accept gaseous feeds. A number of such plasma sources have been developed since the dawn of the accelerator age to generate ion beams for such diverse applications as materials processing, atomic and nuclear physics and heating of fusion plasmas. The following characteristics of an ideal gaseous-feed ion source are of particular importance to AMS:

- Stability (for repeatability of results from sample to sample),
- Efficiency (efficient utilization of a finite-sized sample),
- Low memory effect (to minimise contamination between successive samples).

By a remarkable coincidence, an ion source with many of these characteristics had been developed at the CRL of AECL, but with a very different application in mind. Fortunately, the team at NOSAMS became aware of the ion source work at Chalk River and initiated a series of collaborative experiments to investigate the feasibility of employing the Chalk River ion source technology for on-line AMS.

THE ING PROJECT

The roots of ion source development at Chalk River extend back several decades to a project to develop a successor to the NRU reactor as the prime on-site research facility. In the summer of 1963, a committee under the leadership of G.A. Bartholomew was set up at CRNL to study a high neutron flux facility that would have a flux up to 1000 times that of NRU. The committee quickly settled on a reference design using a high-current linac to serve as a source of high-energy protons for a spallation neutron target. The basic parameters of the accelerator driver for what became known as the Intense Neutron Generator, were set out in 1967 as:

Table 1: ING Accelerator Parameters

Ion Source	Duoplasmatron, 120 mA DC, 70% protons
Injection	750 KV, DC Cockroft-Walton generator
Drift tube linac	106 MeV output Alvarez linac, CW, 110 m long
Coupled cavity linac	1000 MeV output, CW, 1430 m long
Output	1000 MeV, 65 mA CW protons (65 MW beam!)

These parameters were extraordinarily ambitious for the time and would be extremely challenging to meet today after 40 years of development of accelerator components. Perhaps the only contemporary machine that comes close to matching this specification is the Spallation Neutron Source at Oak Ridge [4], with similar beam energy but an average proton beam current of 1.4 mA for a target power of 1.4 MW. The SNS is currently under construction and is scheduled for full-power operation this year.

One of the most severe challenges for ING would have been the injector section, where it is important to accelerate the protons to injection energy before space charge forces disrupt the beam, causing unacceptable beam spill and activation of the structure in the higher-energy sections of the machine. Therefore, an ion source development laboratory was established early during the ING project at Chalk River. Work in this laboratory focussed on the development of proton sources with the capability of supplying the very high beam currents required for ING with the conflicting requirements of low beam emittance (a measurement of the angular dispersion of beam particles with beam radius) and acceptable reliability at high duty factor (DC beam)).

Despite the cancellation of ING by the federal government in 1968, interest was maintained at Chalk River in developing high power, high duty-cycle accelerator structures for industrial applications, fusion and electro-nuclear breeding. To support this work, a vigorous ion source and injector development program continued. By 1991, the low-energy injector section for an ING-like machine was shown to be entirely feasible. By then, the injector had evolved from the to a compact radio frequency quadrupole (RFQ) accelerator with the proton beam supplied by a microwave-driven "ECR" ion source. The basic parameters of this machine are presented in Table 2. With the successful demonstration of the RFQ-1 injector, this work was terminated at Chalk River. The technology developed during this program has been adopted by U.S., European and Japanese laboratories working in the emerging field of accelerator-driven systems for electro-nuclear breeding, sub-critical accelerator-driven reactors and actinide burning [5].

Table 2: RFQ-1 Experiment Parameters

Ion Source	2.45 GHz ECR, 180 mA, >75% protons
Injector	4-vane RFQ, 268 MHz, 250 KW
Output	65 mA @ 600 KV, 55 mA @ 1.2 MeV

THE CHALK RIVER MICROWAVE ION SOURCE

The ion source [6] eventually developed for the RFQ-1 project was specifically designed to have very good reliability during continuous (DC) operation, very high fraction of atomic species in the output beam and good beam quality (low noise and emittance). These qualities were achieved by adopting a process often known as Electron Cyclotron Resonance, or ECR, to generate the requisite hydrogen plasma from which the hydrogen beam is extracted[3]. This process is illustrated schematically in Figure 2. A section view of a compact version of this ion source [7], developed later at CRL, is shown in Figure 3.

With reference to Figures 2 and 3, microwaves at the standard industrial frequency of 2.45 GHz are directed along a tapered waveguide into an evacuated plasma chamber through a ceramic microwave window. The plasma chamber is fabricated from copper or stainless steel and is approximately 50 mm diameter x 50 mm long. A gas inlet near the window admits feed gas at flow rates from 0.01 to 2.5 standard cubic centimetres per minute (sccm). A solenoid magnet imposes a uniform axial magnetic field of approximately 900 G on the chamber volume. Free electrons rotating in the solenoidal magnetic field in the plasma chamber resonantly absorb energy from the microwaves (thus, electron cyclotron resonance), creating a dense plasma close to the microwave window. It is thought that the plasma is ducted along the magnetic field lines to the extraction aperture downstream from the window.

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[3] In fact, the Chalk River ion source was found to operate more efficiently with plasma conditions somewhat different than ECR and is therefore referred to as a "microwave-driven" ion source.

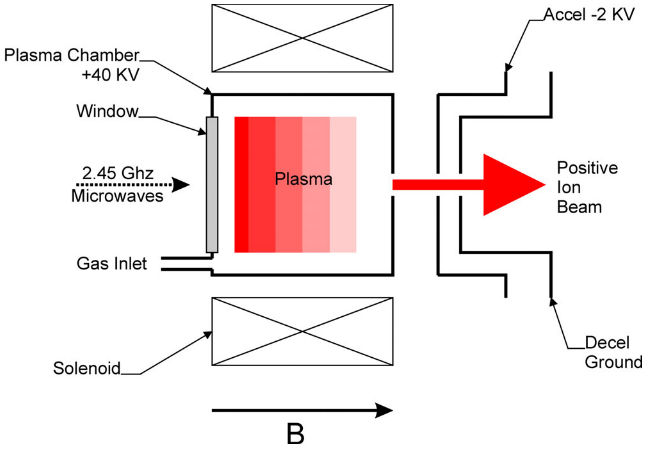

Figure 2: Schematic of Chalk River Microwave Ion Source

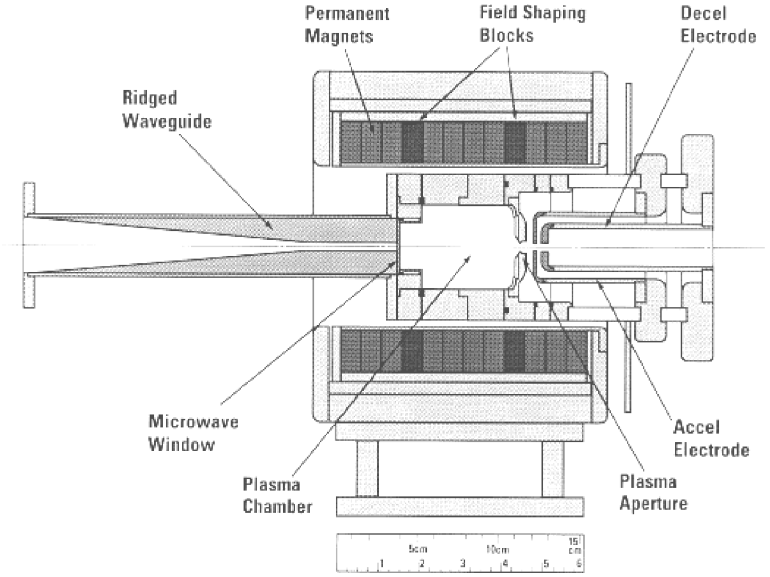

Figure 3: Compact Permanent Magnet Microwave Ion Source

Ions are extracted from the 5 mm diameter plasma aperture and formed into a beam by an electric field established between the plasma chamber and two electrodes with apertures on axis to allow passage of the beam. For the experiments with the compact version of the source reported here, the plasma chamber can be biased at up to +40 kV. The middle “accel” electrode is usually biased negative with respect to ground to provide a barrier against backstreaming electrons formed downstream of the extraction column. The last electrode, the “decel”, is grounded.

The process of plasma formation by resonant absorption of microwaves is efficient. Under favourable circumstances (low gas flow, high RF power and high extraction voltage) as much as 1/3 of the gas entering the plasma chamber is ionised and formed into a beam. This, of course, is a significant advantage when dealing with very small AMS samples, where efficient sample utilization is crucial. The microwave ion source is also intrinsically reliable compared to conventional arc-discharge ion sources, since there are no incandescent filaments in contact with the plasma.

FEASIBILITY STUDIES AT NOSAMS

An intensive program to study the feasibility of the Chalk River microwave ion source for use in AMS has been underway at NOSAMS for the last five years. The experiments there have taken essentially two forms: first, experiments on a test stand to explore such factors as sample memory effects and ability to handle simulated GC effluent under ideal experimental conditions, and second, experiments in which the microwave source is used as an injector for the NOSAMS accelerator to test the stability of the source with real and simulated AMS samples [8, 9]. The ion source used for these experiments is the compact version shown in Figure 3. This version of the source was developed at CRL specifically for use at the TASCC facility, where limitations in the available deck power and extraction voltage had to be accommodated. This version of the source is therefore somewhat limited in beam current compared to the proton source version.

It will be recalled that an AMS accelerator requires a negative ion beam to avoid interference from the ubiquitous ^{14}N contaminant ion. Therefore, an additional stage is required to convert the positive ion beam extracted from the ion source. This conversion is carried out by passing the positive ion beam through a charge exchange canal, a tube having a diameter of approximately 1 cm and length of 10 cm (not unlike the stripper canal in the accelerator terminal). The canal is connected to a heated reservoir containing a material that tends to donate electrons, such as cesium, sodium or magnesium. For the experiments reported here, magnesium vapour was used as the electron donor, requiring the charge exchange canal to be operated at approximately 490°C to produce sufficient target thickness. The conversion efficiency from a C^+ to C^- ions measured on the NOSAMS test stand varies from 8.5% to 15%, similar to published data. The beam lost in conversion must be considered when comparing efficiencies of other types of ion sources.

The latest version of the ion source test stand at Woods Hole is shown schematically in Figure 4.

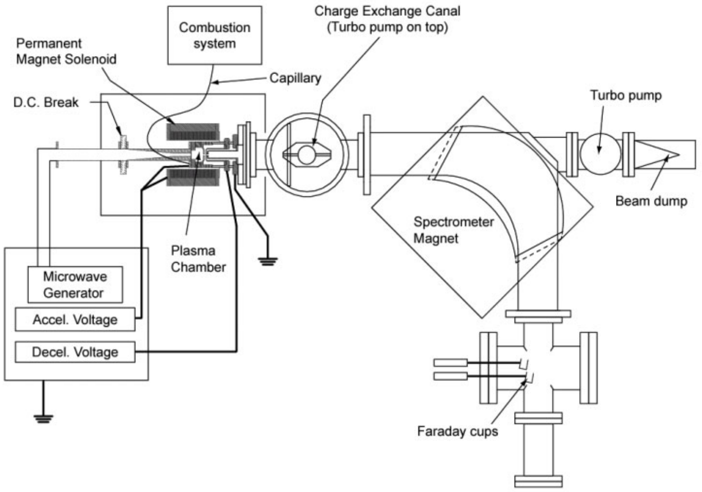

Figure 4: Ion Source Test Stand at NOSAMS

The ion source and charge exchange canal are mounted to a vacuum chamber pumped by a turbomolecular pump to a base pressure of 10^{-6} Torr. A 90° spectrometer magnet with a large vertical gap separates the accelerated beam into atomic and molecular species, which can be measured on faraday cups at the magnet exit. The test stand can characterize the positive ion beam extracted from the microwave source, or, by heating the charge exchange canal and reversing the mass spectrometer magnet polarity, the negative ion beam can be analysed.

The results of a test stand experiment to observe the steady-state characteristics of the ion source are shown in Figure 5. The source was operated with pure CO_2 at a flow rate of 240 µL/min to simulate the flow of analyte from a gas chromatograph. The positive ion spectrum (upper trace) illustrates the break-up of the CO_2 feed into atomic and molecular species. Analysed C^+ ion currents of 400 µA were obtained at an extraction voltage of 30 KV and a microwave power of 125 Watts. With the charge-exchange canal operating, a negative ion spectrum is obtained (lower trace) showing C^- currents of 63 µA. Also apparent in this figure is the production of intermediate-energy ions through break-up of molecular ions in the acceleration gap. These results imply a global efficiency for the ion source and test stand beam transport of 2.3% for the conversion of CO_2 feed gas molecules into C^+ ions and an overall efficiency of 0.4% for the conversion of CO_2 molecules into C^- ions. It is thought that these efficiencies can be improved by better coupling of the ion source to the charge exchange canal (which is not at present optimised) and by operating the source at higher microwave power and extraction voltage.

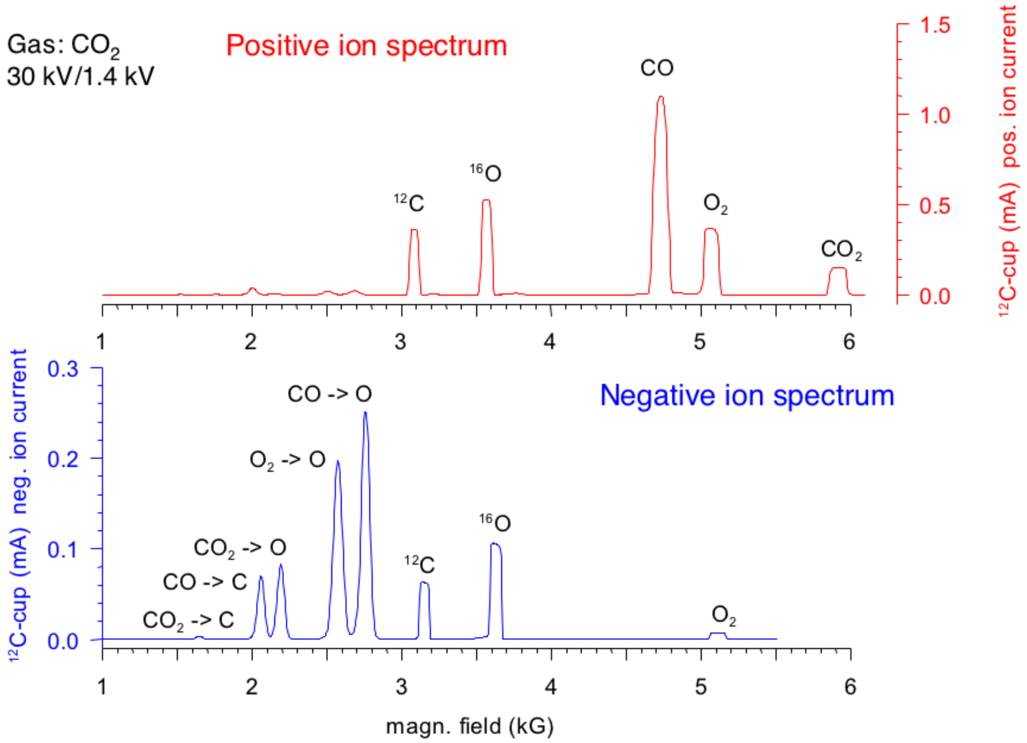

Figure 5: Positive and Negative Ion Spectra Obtained on the Woods Hole Test Stand

The microwave ion source has also been operated as an injector for the NOSAMS tandem accelerator by installing it temporarily in place of one of the standard sputter sources. Unfortunately, the angular divergence of the ion beam was large compared to the beam from the sputter source. To suppress scattered ions, a beam-limiting aperture of 5 mm diameter was installed at the object point of the injector. Even with this limitation and the mismatch of the beam to the ion optics of the recombinator section, C^- beam currents of 22 µA were obtained at the entrance to the accelerator when the ion source was operated on pure CO_2 feed gas.

In order to test the response of the microwave ion source for sample memory and other dynamical effects, a special gas handling system was devised to rapidly switch a feed gas stream containing ^{14}C with "radiocarbon dead" CO_2. The isotopic ratios of carbon were measured as described earlier. A typical result is shown in Figure 6, in which the observed $^{14}C/^{12}C$ ratio is plotted during the transition from ^{14}C "live" to "dead" feed gas. The absence of significant sample retention time is evident. "Live" CO_2 gas samples were obtained from combusted oxalic acid samples[4] and fermenting beer supplied by a WHOI staff scientist (see Figure 7). The fraction modern[5] for the beer gas was 1.068, consistent with off gassing from recently harvested organic matter. System background counts were as low as are normally observed with the conventional sputter sources.

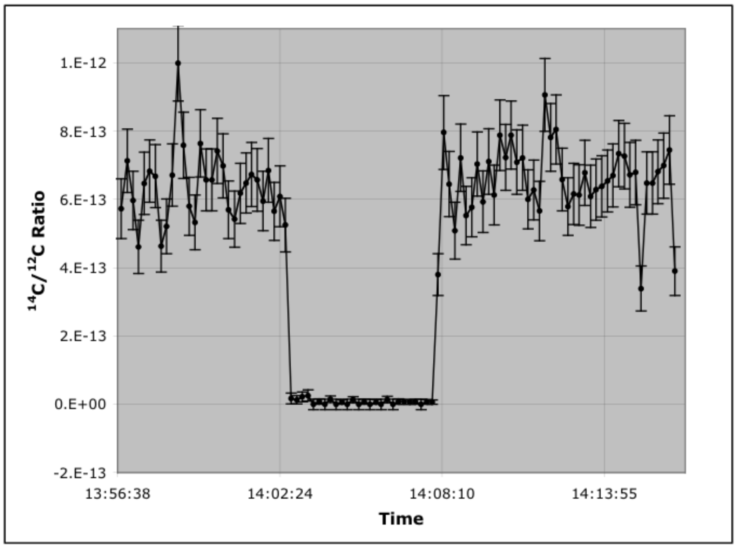

Figure 6: Sample Memory Experiment

Figure 7: "Live" CO_2 Sample

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[4] Oxalic acid standards provide a "modern" calibration standard for AMS measurements. The original oxalic acid standard was manufactured from a crop of 1955 sugar beet. This standard is no longer commercially available and has been superseded by the standard HOx 2, which was manufactured in 1977 from a crop of French beet molasses.

[5] Modern samples are arbitrarily defined as having a date of 1950 (before atmospheric nuclear weapons testing injected an extra source of ^{14}C into the atmosphere). Thus, a sample of material that was in equilibrium with the atmosphere after 1950, can have a radiocarbon date younger than "modern".

2. Discussion

What do the current results say about the potential for AMS with the microwave source? Recall that the AMS system determines the age of a sample by measuring the ratio of ^{14}C to ^{12}C ions collected, thus:

$$R = \frac{{}^{14}C}{{}^{12}C}$$

and the error in the ratio is given by:

$$\frac{\sigma_R}{R} = \sqrt{\frac{1}{{}^{14}n} + \frac{1}{{}^{12}n}} \approx \sqrt{\frac{1}{{}^{14}n}}$$

(the error is dominated by the number of ^{14}C counts).

It follows that to achieve a 10% uncertainty in the measurement, we need to collect 100 ^{14}C ions at the detector. For a half-modern sample, this implies that 2 x 10^{12} ^{12}C ions are collected at the high-energy faraday cup. Using the figure obtained on the test stand of 0.4% as the global efficiency of $^{12}C^-$ ions generated per molecule of CO_2 gas admitted to the source and further assuming a 50% transmission efficiency of C^- ions through the stripper canal and beam transport of the accelerator, 1 x 10^{17} CO_2 molecules (0.2 µmoles of CO_2 gas, equivalent to 3.7 µL CO_2 or 2 µg carbon) must be admitted to the source during the counting period to achieve this uncertainty.

At the present CO_2 gas flow rate of 240 µL/min required to sustain the ion source plasma, the analysed sample would be present at the detector for approximately 1 second. This count rate is not incompatible with the existing detector. The timing of the gas pulse is also similar to the expected shape of an analyte pulse from a gas chromatograph. Compared to the state-of-the-art sample size of approximately 20 µg carbon required for a conventional sputter source target, these predictions are very promising, but at present represent extrapolations from test stand data and remain to be confirmed by experience with real samples. On the other hand, we also expect to improve the efficiency of the ion source/charge exchange canal system, as described later.

The results outlined here have encouraged us to proceed with the design of a new version of the microwave driven ion source optimized for continuous flow AMS. The new source will deliver a beam to a new accelerator facility specifically designed to handle the high-current, divergent beam from the microwave source and charge exchange canal. These developments are discussed in the next section.

AN OPTIMISED ION SOURCE FOR CONTINUOUS-FLOW AMS

The new ion source design will incorporate several improvements that specifically address the requirements for an AMS facility. These include:

- Better coupling of the extracted positive ion beam to the charge exchange canal,
- Improved control of the plasma chamber magnetic field,
- Ability to reliably operate at higher extraction voltages,
- Suppression of sources of outgassing into the vacuum system, including the elimination of as many O-ring seals as possible (especially water seals).

In order to optimize the coupling of the positive ion beam to the charge exchange canal, extensive modelling of the positive and negative ion beam was carried out with the code SIMION[6]. A typical SIMION output is shown in Figure 8, in which a novel biasing scheme is illustrated. Instead of biasing the plasma chamber positive, the ion source is essentially at ground potential and the charge exchange canal is biased negative (in this case, -30 KV). The conducting boundaries of the ion source, electrodes and charge exchange canal are shown in brown and electrostatic equi-potentials are shown in black. The positive ion beam (not shown) is thus extracted into the canal from which the charge-exchanged beam (red) is ejected at 60 KV energy, not unlike a miniature Tandem accelerator. The higher beam energy is advantageous, since the relative energy spread from energy straggling in the charge exchange canal is reduced by the factor 60 KV/30 KV. A three-element electrostatic lens (einzel lens) downstream of the charge exchange canal focuses the negative ion beam into the accelerator beam line.

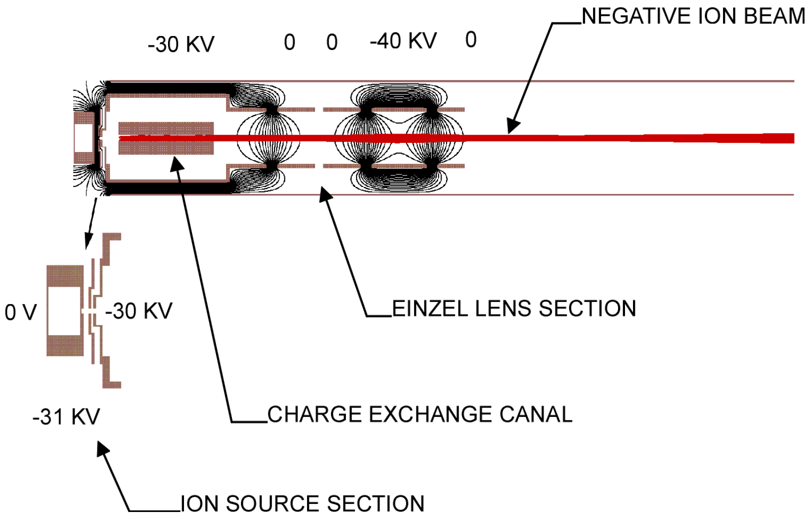

Figure 8: SIMION Simulation of Biased Charge Exchange Canal

The mechanical design of the new ion source is presently being undertaken by the Mechanical Equipment and Seal Development Branch at Chalk River. The present design concept is illustrated in the section view shown in Figure 9, modelled in Solid Edge[7] mechanical design software. Compared to the earlier version of the source shown in Figure 3, the new arrangement features a re-entrant design of the plasma chamber, allowing beam extraction apertures to be positioned as close as possible to the biased charge exchange canal. Extensive use is made of welded and brazed joints to reduce the potential for outgassing and water leaks into the vacuum chamber. The axial magnetic field will be provided by electric solenoids surrounding the plasma chamber (not shown in the figure).

The concept of a biased charge exchange canal has certain practical advantages compared to the previous arrangement, particularly in terms of safety of operation, since all components at high voltage are now enclosed by the vacuum system. Personnel barriers surrounding the plasma chamber and microwave drive components will no longer be necessary.

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[7] UGS, 5800 Granite Parkway, Suite 600 Plano, TX 75024, USA.

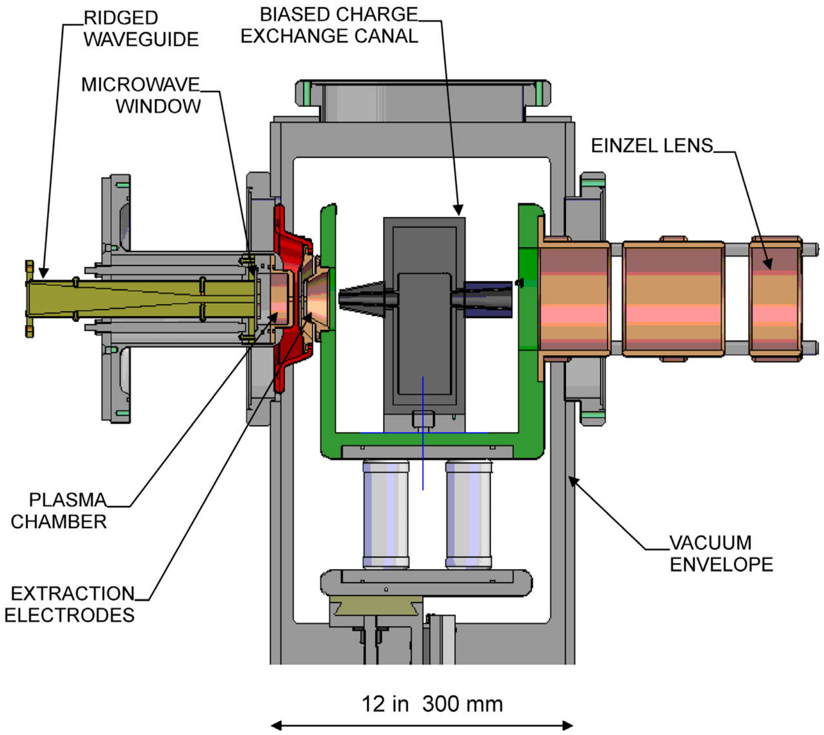

Figure 9: Mechanical Arrangement of New AMS Ion Source. Note that the plasma chamber support insulator and solenoids have been omitted from this view for clarity.

FUTURE DEVELOPMENTS

The introduction of a gas-fed, continuous-flow ion source capable of interfacing directly with the flow of analyte from a gas chromatograph is expected to open rich new fields of study in ocean sciences at NOSAMS. These new possibilities can be broadly divided into two groups. First, one would still deal with discrete gas samples, derived from well-defined sample materials, but with the capability of dealing with multiple samples. These samples could be surveyed rapidly for radiocarbon content with limited precision. Some examples of multi-sample surveys include:

- Identifying the sources of organic materials in marine sediments. One would develop a matrix of chemical structure with isotopic abundances (C^{13} and C^{14}) to identify terrestrial plant products, lipids from biological processes, erosion products and petroleum products.
- Surveying recycled organic matter in shales and sediments. Bacterial products from ancient deposits would be C^{14} free. When ancient shales are eroded and the organic materials are incorporated into the modern carbon cycle, the ancient carbon must be separated from modern sources. Pyrolysis and thermal-release can be used to do this. The various temperature fractions will yield different ratios of modern to dead carbon.
- Investigation of bacteria colonies at petroleum and gas-hydrate seeps. Huge colonies of bacteria are found at these seeps. They feed on the petroleum, methane and organic detritus. Each of these three sources has its' own isotopic signature discernable by AMS measurements.

Preliminary work on the "front-end" techniques for multi-sample investigations has been carried out at NOSAMS and may be mentioned briefly here. A combined thermal pyrolysis and combustion device is being developed to analyze sediment samples by heating them in a programmed fashion. This releases or decomposes the mixture into various temperature fractions, which then pass through a hot copper-oxide combustion stage, to generate CO_2. Preliminary tests have been performed with bicarbonate samples.

Second, the varying radiocarbon content of a continuously flowing stream of analyte could be analysed, such as might be obtained from an on-line gas chromatograph or continuous combustion device. Some examples of studies utilizing this technique include:

- Thermal ablation of an ice core. At the University of Arizona, a method of continuously ablating an ice core to sample it has been developed. One could think of doing this online to a continuous flow AMS system, and analyzing the CO_2 as it is released from the ice core. Measurements of annual CO_2 levels in ice cores, going back over 100,000 years, have shown that we are presently exceeding any previously known historical levels in the atmosphere.
- Any method that generates CO_2 continuously from a substrate or combustion process, or even a fermentation process, could be coupled directly to the continuous flow AMS system to provide a radiocarbon profile. Acid decomposition of carbonates, which produces CO_2 is an example. Bacterial digestion of a substrate is another.
- The "moving wire" device, which has been developed both at Woods Hole Oceanographic Institute and is now in use elsewhere. This is used with liquid chromatography, in which the liquid effluent is sprayed on a wire, which then passes through a combustion volume, where evolved CO_2 is trapped and could be carried into the continuous flow AMS system. Liquid chromatography is used for separation of heavy molecules, which may be too large for a gas chromatograph to handle.
- Laser ablation or a plasma torch pyrolysis of a sediment cores. Organic residues from an oil spill embedded in a sediment core could generate a radiocarbon profile in which the radiocarbon “dead” spot would locate the residue from the oil spill.

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