TARGET PREPARATION FOR CONTINUOUS FLOW ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. For very small samples, it is difficult to prepare graphitic targets that will yield a useful and steady sputtered ion beam. Working with materials separated by preparative capillary gas chromatography, we have succeeded with amounts as small as 20 µg C. This seems to be a practical limit, as it involves 1) multiple chromatographic runs with trapping of effluent fractions, 2) recovery and combustion of the fractions, 3) graphitization and 4) compression of the resultant graphite/cobalt matrix into a good sputter target. Through such slow and intricate work, radiocarbon ages of lignin derivatives and hydrocarbons from coastal sediments have been determined. If this could be accomplished as an "online" measurement by flowing the analytes directly into a microwave gas ion source, with a carrier gas, then the number of processing steps could be minimized. Such a system would be useful not just for chromatographic effluents, but for any gaseous material, such as CO_2 produced from carbonates. We describe tests using such an ion source.

INTRODUCTION

The AMS (accelerator mass spectrometry) system at Woods Hole utilizes a solid-sample sputter source to produce negative carbon ions for injection into the tandem accelerator. The sputtering process uses a primary beam of accelerated cesium ions that impinges upon the surface of a graphite sample. Secondary negative ions are ejected from the surface and extracted to form a beam that is then accelerated. Samples are formed by converting CO_2 to graphite at high temperature. We use equal weights of carbon and iron powder in the sample-catalyst mixture. This method has been used to obtain ^{14}C concentrations for all of our WOCE seawater samples. The amount of graphite used for the solid targets is *ca.* 1 mg, and the precision is accordingly excellent (4‰). Such consistent results are possible only when sample sizes are optimal and output currents uniform. The analyzed carbon ion currents in this program have ranged from 20 to 30 µA.

For arbitrary samples smaller than 50 µg C, it is often difficult to prepare graphitic targets that will yield a useful ion current. Working with materials separated by preparative capillary gas chromatography (PCGC), we have succeeded with amounts as small as 20 µg C (Eglinton *et al.* 1996; Pearson *et al.* 1998). This seems to be a limit and involves 1) multiple chromatographic runs with trapping of effluent fractions, 2) recovery and combustion of the fractions, 3) graphitization and 4) acceptance of reduced precision. Through such slow and intricate work, ^{14}C ages of lignin derivatives and of hydrocarbons from coastal sediments have been determined (Eglinton *et al.* 1997). Such results are attracting considerable interest, but the technique would benefit from improvement and simplification. This could be accomplished completely by abandoning stepwise processing and creating an "online" system in which analytes flow directly and continuously from a gas chromatograph to an accelerator mass spectrometer capable of accepting gas-phase samples. Such a source would be useful for the analysis not only of chromatographic effluents but of any gaseous material, for example CO_2 produced from carbonates. It is hoped that this would avoid the variability in homogeneity, size, current yield, surface conditions and catalyst ratio that are present in solid sputter targets.

Both gas-fed sputter ion sources and true plasma ion sources have been investigated over the years. Early work on a CO_2-fed sputter source at the University of Pennsylvania in the 1980s (Middleton, Klein and Fink 1989) led to the present Oxford University CO_2 ion source, which was the first successful hybrid source in routine operation (Ramsey and Hedges 1997). The gas sample is injected into a helium stream, which flows through a hollow cathode and over a solid titanium button. A portion of the CO_2 is adsorbed on the metal surface and is sputtered by a high-intensity cesium beam. Although the resulting carbon ion beam does not exceed 10 μA, 40-min measurements can yield 0.5% precision with 0.5% background. A commercial ion source of this general type is now produced by National Electrostatics Corporation (Graber Road, Middleton, Wisconsin, USA) in which multiple CO_2 reservoirs are coupled to multiple titanium cathodes. Analyzed carbon ion beams of 13 μA are reported (Shibata *et al.* 1997). In all of these hybrid sources, the titanium buttons are replaced for each sample. Although the ion source utilizes a gas sample, it thus retains the characteristics of batch rather than continuous flow operation.

Historically, negative ions were obtained from the plasma discharge in hot filament-excited duoplasmatron sources. By using an offset aperture, it is possible to extract negative ions from the plasma discharge in this type of source. Usually used for H^- production, it has also been used for production of CN^- ions. Before AMS was developed, mass spectrometric analyses of ^{14}C were attempted using a hollow-cathode duoplasmatron source with $^{15}N_2$ as the carrier gas, which leads to formation of the mass 29 negative ion $^{14}C^{15}N^-$ (Anbar 1978). These beams were not stable enough to be useful.

We have concentrated on a microwave plasma ion source, because of the stability and cleanliness it offers. These positive ion sources operate with a steady, 2.45 Ghz microwave-driven plasma. The plasma is efficiently produced from a carrier gas (such as argon) that flows into the plasma chamber at a constant rate. The extracted beam is dominated by current from the carrier gas, so a large dynamic range of sample sizes (which in practice would form a small fraction of the total flow rate) is not expected to perturb the source emittance characteristics. Because it produces positive ions, an additional alkali vapor charge exchange cell is necessary to convert positive to negative ions.

The compact, permanent-magnet microwave ion source (Wills *et al.* 1998) presently under development at the Chalk River laboratories of AECL (Atomic Energy of Canada Limited) shows promise as a candidate for AMS injection. It was designed to produce high currents (40 mA) of protons, and has recently been optimized for heavy ions. In an earlier (March 1996) collaborative experiment (Schneider *et al.* 1997) we were able to obtain usable amounts of carbon ions by injecting 1-μmol pulses of CO_2 or CH_4. The efficiency of producing singly charged $^{12}C^+$ ions was determined to be 14%. The present account describes further tests made in February 1997. Only a limited time was available to us, because of the imminent shutdown of the AECL accelerator facility.

METHODS

AMS is a ratiometric technique, where samples are compared with standards in a consistent protocol. It is important to present equal quantities of both in an alternating sequence, much like a stable isotope ratio mass spectrometer. The precision of an isotopic analysis is controlled by the number of particles collected at the detector. For the ratio $R = {}^{14}C/{}^{12}C$, we can write

$$(\sigma_R/R)^2 = (1/N_{12} + 1/N_{14}) \qquad (1)$$

where σ is the standard deviation and N is the number of ions collected during measurement of the two isotopes (assuming Poisson counting statistics, σ is equal to the square root of the number of counts). Since ^{12}C is at least 10^{12} times more abundant, the analytical precision is dominated by N_{14},

the number of detected ^{14}C ions. If we define E as the overall detection efficiency of the system, (ions detected)/(molecules introduced to the ion source), then

$$N_{14} = mEN_AR \qquad (2)$$

where m (moles) is the amount of sample gas introduced into the ion source, and N_A is Avogadro's number. To obtain $\sigma_R/R = 0.03$ (equivalent to 30‰ in the measurement of Δ^{14}C), we need only 0.4 μmol CO_2 if $E = 0.01$, a value typical for present AMS systems. Peaks of 20 sec duration and containing 0.4 μmol C can presently be generated by conventional "megabore" capillary columns (0.53 mm inner diameter, 0.5 μm stationary phase thickness) during a single gas chromatographic run. Loadings in excess of 1 μmol C are likely to be possible with newly available "multicapillary" columns. To introduce small quantities of gas into the microwave plasma source, a carrier gas is necessary to keep the plasma ignited and steady. It is also convenient to utilize capillaries that can maintain laminar flow across pressure gradients, and in the case of silica capillaries, traverse high voltage gradients. We chose to use argon as the carrier gas for several reasons. It will sustain the microwave plasma at flow rates of *ca.* 0.2 mL min^{-1}, it is readily obtainable in high purity and its ions are readily discriminated from those formed from the CO_2 in the sample. We constructed a test injector based on principles developed by Merritt, Brand and Hayes (1994) shown in schematic view in Figure 1. By simply inserting the plunger, one is able to start and stop the sample gas flow, thus entraining a pulse of sample gas in the flow of argon carrier gas without causing a pressure transient in the gas flowing into the ion source.
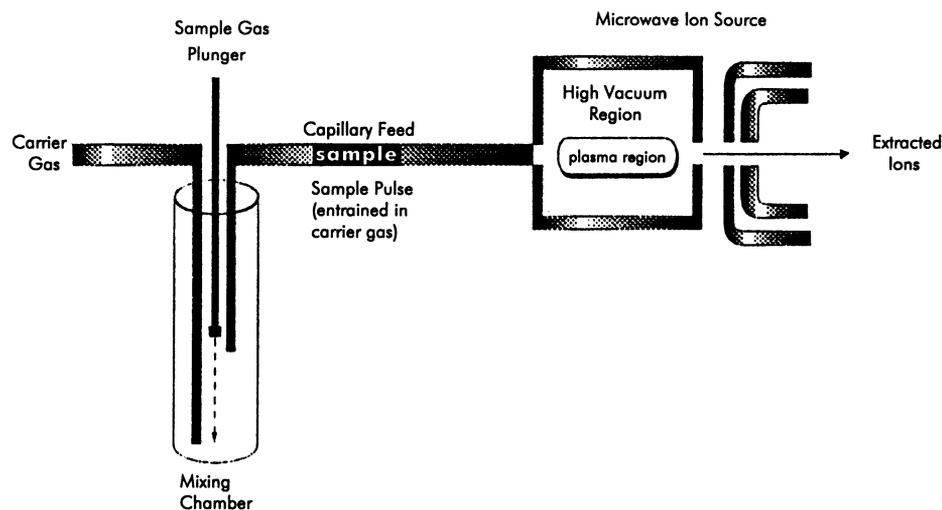
Fig. 1. Test device for injecting pulses of a sample gas into a carrier gas stream, and then into the microwave ion source. A continuous flow of carrier gas fills the mixing chamber, which is open to atmosphere at the top. When the plunger (a hypodermic needle) is depressed, the sample gas is mixed into the flow of carrier gas and is intercepted by the pickup capillary. Because this device is open, no pressure transient is introduced into the gas flow. Rectangular pulses of CO_2 are produced with a flow rate of *ca.* 0.2 mL min^{-1}. A 75 cm length of 0.11 mm deactivated silica capillary leads to the ion source.

Before the test pulses were introduced into the ion source, they were observed with a residual gas analyzer to verify pulse shape, permitting subsequent comparison with the shape of the resulting ion current pulse. Figure 2 shows the negative carbon ion current pulse, resulting from the injection of a 4-min-long pulse of sample gas into the ion source, followed by a charge exchange cell. *Ca.* 0.8 mL of CO_2 was injected. The gas pulse had a rectangular shape, and the ion pulse showed an extended time constant for buildup and decay.
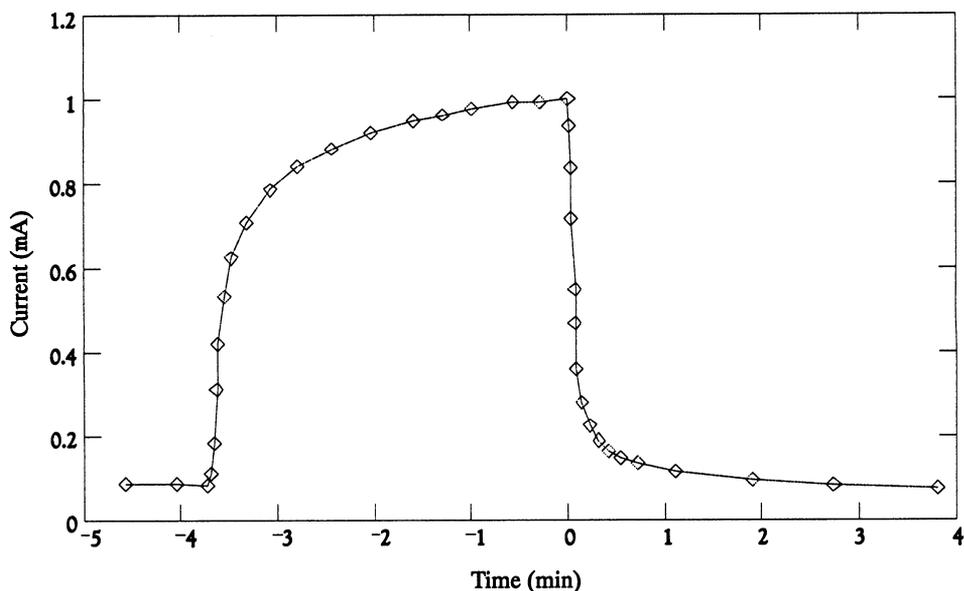
Fig. 2. A negative ^{12}C ion current pulse obtained from the microwave plasma ion source, followed by a charge exchange cell. Carbon dioxide was injected with the test pulse injector of Figure 1. The pulse duration was 4 min.

To inject sample and reference gas aliquots alternately, or in some well-defined sequence, we built a second device which makes use of two sample loops that can be switched in and out of the carrier gas feed. For this purpose we utilized a switching valve (Valco Instruments, Houston, Texas) that accepts sample loops of arbitrary size, made of 0.8 mm stainless tubing. We made two loops, 10 cm and 30 cm long, having volumes of 50 μL and 150 μL, respectively. The setup is shown in Figure 3.

We cycled the remotely actuated valve numerous times, with both argon and CO_2 gas pulses. We also varied the switching time from 30 s up to several minutes. From the analyzed spectra, we recorded current pulses for argon, oxygen, CO and carbon. The shapes of the pulses were similar,
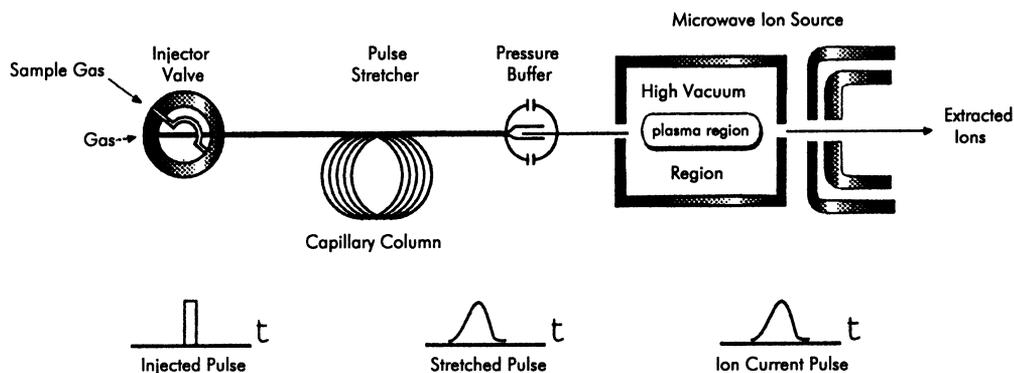
Fig. 3. Test device for loop injection into a microwave plasma ion source. One of two sample loops is shown; these inject samples into the carrier gas when the valve is rotated. The capillary column, 27 m of 0.32 mm silica capillary, is used to stretch out the pulse in time and the pressure buffer is an open split (*e.g.*, Merritt *et al.* 1995), which removes pressure transients. The final capillary is 75 cm of 0.11 mm deactivated silica, as in Figure 1.

but of course the intensities changed, according to the fraction of the total ion current carried by the species monitored. A typical pulse shape, from a chart recorder trace, is shown in Figure 4. The ratio of the areas under the two pulses is 2.3 to 1. The failure of the integrated ion currents to reach the expected 3-to-1 ratio is probably caused by flow restrictions leading to pressure differences in the two loops.
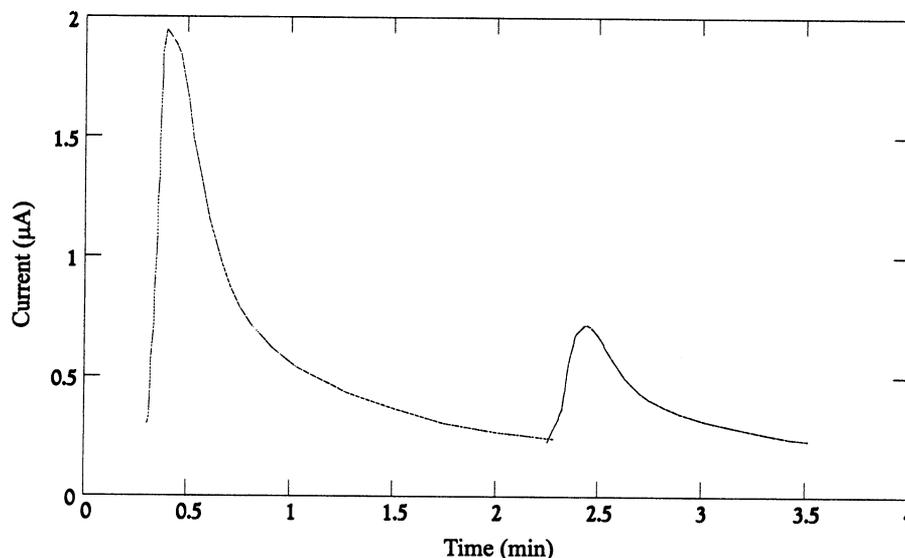
Fig. 4. Negative ^{12}C current pulses from 50 and 150 μL sample loops, injected 2 min apart. These pulses were recorded in a Faraday cup following magnetic analysis.

RESULTS

Evidently a significant time constant is involved for the ion current to reach equilibrium, both at the beginning and end of the pulses. To compare the ion current pulse with the original injected gas pulse, we superimposed the tails of the residual gas analyzer pulse and the test pulse of Figure 2. This comparison is shown in Figure 5.

Some holdup time in the ion source would be expected. As molecules are released into the vacuum of the ion source volume, they have a mean free path of about 1 m for CO_2 and 10 m for argon. Adsorption on the walls of the chamber would occur immediately. Sorption and desorption of sample gas within the ion source and on the surfaces within the gas handling system probably accounts for this tailing. The longer tail associated with the plasma source indicates higher binding energies in that device, probably due to chemisorption or transient implantation of energetic particles in surfaces within it.

We also decomposed the tail of the ion current pulse to try to determine its origin. We tried to fit various functions to it, such as exponential, and inverse powers of time. Figure 6 shows a fit with two terms, an initial exponential decay having a 3 s time constant, and a diffusion term, having a $(t^{-0.5})$ dependence. This combination seemed to give the best fit.

The volume of the Chalk River microwave ion source plasma chamber was 137 cc for these tests, with an extraction aperture of 2.5 mm. The silica capillary was adapted to a 20-cm-long, 6-mm-diameter stainless steel feed tube, brazed into the source body, next to the microwave window. The
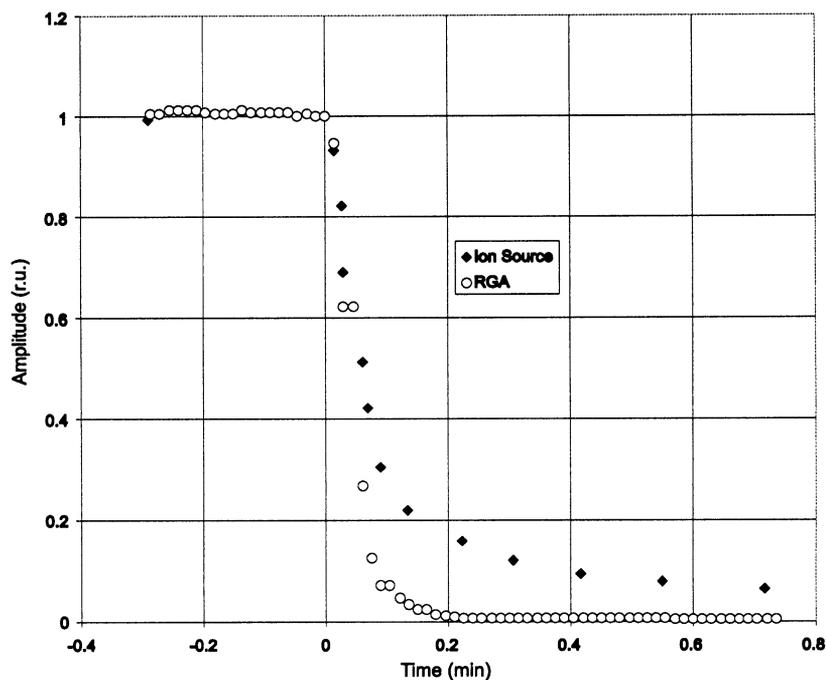
Fig. 5. Superposition of the tails of the ion pulse and gas pulse for mass 12. The gas pulse has a decay constant of 2.4 s, and the ion pulse is 3 s. Both pulses had a 4 min width.
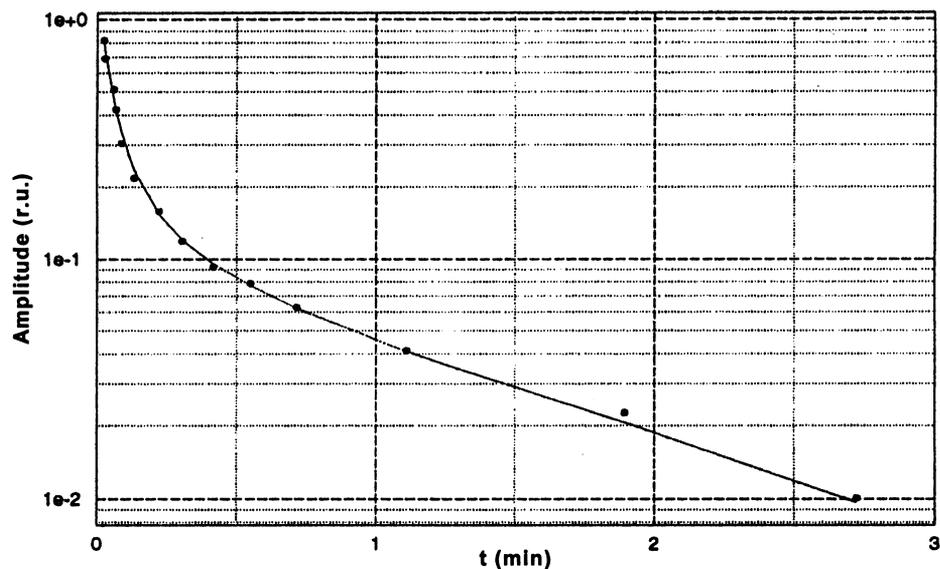
Fig. 6. Ion current tail, after turning off the gas pulse. The analyzed ^{12}C current decays initially with an exponential time constant of 3.06 s. The longer component is fitted well by a diffusion term having a diffusion coefficient of 0.684 cm^2 min^{-1}. The complete expression is $f(t) = a + b \times \exp(-t/\tau) + c/(4\pi Dt)^{0.5}$, where $a = -0.0455$, $b = 0.459$, $c = 0.267$, $\tau = 3.06$ s and $D = 0.684$ cm^2 min^{-1}.

nearest pressure sensor was downstream of the extraction region and read 5×10^{-6} mb. Although the source body was copper, the interior of the plasma chamber was lined with boron nitride. A large surface area was therefore available for adsorption of the gas, and is partly responsible for the long decay time. Using the diffusion constant estimated above, in 3 minutes' time a gas volume 2.7 cm in diameter would evolve, which is commensurate with the dead volume of the feed tube, plus about 5% of the source cavity, which may see only a weak RF field. With further testing, we would hope to minimize desorption and diffusion times by reducing the volume, removing the liner and the original 6 mm feed tube. In addition, the inside surfaces could be silver plated to minimize sticking of the gas molecules. The test that was carried out in 1996, without the boron nitride liner, appeared to have a faster decay time (<1 s), although few pulses were actually recorded.

CONCLUSION

Despite the limited time available for testing, and the subsequent closure of the AECL accelerator facility, we are optimistic that further work can show that a high-efficiency microwave ion source with capillary gas injector will be useful for AMS applications. This source, with its permanent magnet array, requires RF power levels of only ~200 W. The efficiency is very high: the fraction of singly charged carbon ions produced, per atom introduced into the source, is 14%. (Compare this to the efficiency of an inductively coupled plasma source, on the order of parts per million.) At present, we have requested a loan of the ion source for continued testing at Woods Hole. Because the cycle times of typical gas chromatographic runs using capillary columns are *ca.* 60 min, it seems unwise to begin by placing such a device online to the AMS ion source. Instantaneous sample flow rates would exceed 1 µmol C min^{-1} for only portions of a chromatogram. While large bore and multicapillary columns are being developed, permitting higher sample loadings, it seems easier to start with carbonates, such as corals or foraminifera, where a 10 mg sample of calcium carbonate could yield flow rates of 10 µmol (0.22 mL) per minute for 10 min. Using the 14% computed efficiency of ion formation and extraction for the present microwave ion source (Schneider *et al.* 1997), one would expect 2.4 mA of positive carbon ion current. Subsequent conversion to negative ions for injection into the tandem accelerator could be as low as 5%, depending on charge exchange canal technology. This would yield a minimal 120 µA of negative ion current. Over the 10 min duration of this gas sample, one could then collect 200,000 ^{14}C counts from a modern sample. Such a 2‰ measurement is already useful, but improvements in charge exchange yield would be highly desirable.

ACKNOWLEDGMENTS

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