

RADIOCARBON DATING BY ION COUNTING: PROPOSALS AND PROGRESS

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ABSTRACT. In the two years since the first successful measurements of ^{14}C by high energy mass spectrometry, the advantages and the basic techniques of the method have been sufficiently reported. They will not be repeated here. This paper describes the work being done at Oxford to fill the gap between demonstrating the effectiveness of the approach and the creation of a facility dedicated to the carbon dating of milligram samples.

The high energy mass spectrometer

The spectrometer is based on the General Ionex 3 MV Tandetron. Earlier work at Oxford (Barratt and others, 1978) confirmed theoretical expectations that the advantages of mass spectrometry using nuclear physics particle identification techniques would be lost below a final carbon ion energy of 8-10 MeV, and that a terminal voltage of 2.5 MV was the smallest size of accelerator before performance was compromised. At this voltage, stripping of C^- to C^{3+} is maximized, and we saw no evidence for formation of CH^{3+} , unlike the detection of CH^{2+} by the Rochester/Toronto group. The Tandetron, with its parallel-fed Cockroft-Walton-type power supply in place of a moving charged belt, was chosen mainly because of its higher current capability. We believe this will help ensure greater stability of transmission of the ion beams. The other active components of the beam transport system are shown in figure 1. They are based on the successful experiments made with the Oxford EN tandem. The acceptance of the system as a whole, which, in our case, is limited by the magnet sizes and accelerator tubes, is designed to transmit all of the beam generated at the ion source except for a small fraction of halo. The inflector magnet is a 90° double focusing type, with a resolution matched to the energy spread in the beam produced by the source. Most of the injected beam at mass 14 will, of course, consist of $^{13}\text{CH}^-$ and $^{12}\text{CH}_2^-$; nevertheless, it is worthwhile to exclude 'tails' due to neighboring mass peaks, such as $^{14}\text{NH}^-$, and limit the injection of particles derived from energy changing collisions in the magnet region. The ultimate detection of ^{14}C ions is by a gas counter filled with a few Torr of iso-butane, and a data collection system similar to that employed in the EN tandem experiments. In this detector, the energy loss of each particle is measured over two regions (after the particle has traversed a $\frac{1}{2}$ micron window), while the residual energy and the total energy (as a check) can all be measured. We do not believe it advantageous to collect positional information on each particle. The performance of this detector with the EN suggests that it could reliably discriminate ^{14}C from an extremely high background level of other ions of similar magnetic rigidity, and that the limitation to the system is the excessive count rate caused by such a high background. Accordingly, a Wien filter with a fairly low resolution (about 5 percent in velocity) is used to reduce

the count rate. We expect that, for modern samples, ^{14}C will constitute the predominant fraction of the beam entering the counter.

While this arrangement might allow us to detect ^{14}C down to levels of $10^{-16-18} \times ^{12}\text{C}$, (where the ^{14}C count rate statistics are likely to be the ultimate limitation) it is equally important for carbon dating to make an abundance ratio measurement to high accuracy.

The main sources of instability in the system come from the ion source operation, and the accelerator and stripper. Since the ratio of ^{12}C and ^{14}C beam currents are to be determined, systematic errors are minimized by treating the two ion beams as similarly as possible, and by comparison with standards. Since the ^{12}C beam is some 10^{12} times as intense, it must be reduced before acceleration. This reduction could be in amplitude, but we believe there is less of a problem in reducing the time average of ^{12}C by arranging for its transmission in short bursts, eg, of $50\mu\text{sec}$ duration (although longer pulses are also possible) at a repetition rate of several Hz. The same arrangement can be made for ^{13}C , so that any mass dependent change in the transmission can be anticipated, while a separate measurement of the stable isotope ratio of the sample can also be made. This might check for any fractionation brought about in the sample chemistry. The pulsing of the beams is achieved by varying the energy of the beam through the inflector magnet, so that the desired isotope is always deflected by 90° . The collection cups for measuring the stable isotope current must be designed for very stable performance, with attention given to secondary ion and electron emission, photo-ionization, back-scattering, etc. A further source of error is the presence of short-lived ions, eg, metastable C^- , whose decay might be collisionally controlled. Many of these effects can only

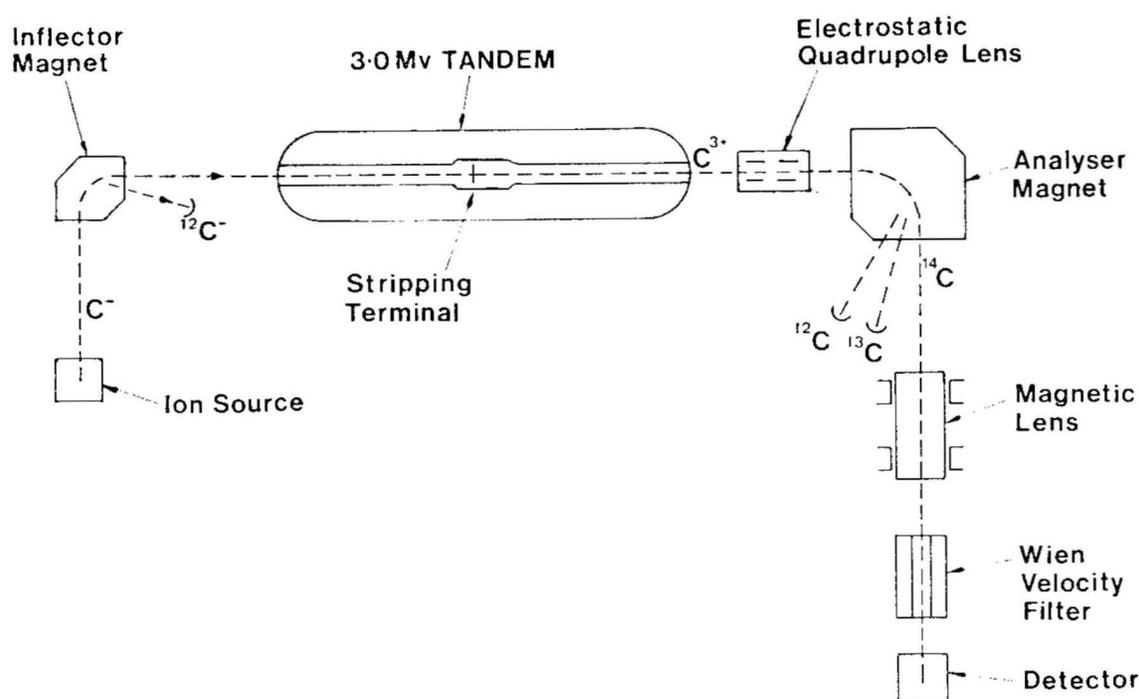


Fig 1.

be studied when a high precision accelerator/mass-spectrometer is available. Taking into account the reported accuracy of the Rochester/Toronto group dates of 1 to 5 percent, without any elaborate procedure for the elimination of systematic error, there seems no reason why machine errors cannot be reduced to below at least $\frac{1}{2}$ percent. At this level of accuracy, other aspects of the system, the ion source, sample preparation, to say nothing of the integrity of the sample itself, must all be taken into consideration. At better than $\frac{1}{2}$ percent accuracy, the accumulated ^{14}C count is also important in determining the count rate statistical error, and it is clear that this will set an ultimate limit of 0.1 percent and, perhaps, a practical limit of about 0.2 percent on the ratio measurement.

Ion source development

Ion source performance is crucial to the operation of the whole system. To obtain sufficient ^{14}C counts in a reasonable time, a current of at least $10\mu\text{A C}^-$ must be generated, while for high precision, eg, 10^6 counts, or for very old samples, much higher currents, eg, $50\mu\text{A}$, are desirable. These high currents must be achieved without increasing the beam emittance. To minimize systematic errors, the amplitude stability should be better than 1 percent over the relevant frequency ranges, while any isotopic fractionation in the source should be small and, above all, reproducible. Other requirements are negligible memory and cross contamination effects, and finally, convenience of sample handling.

Virtually all the work done so far with C^- has employed a caesium sputter source using solid samples. We have found the back-reflected version of this source to be especially suitable for this application, and have made a careful study using an experimental test-bench as well as computer simulation to understand and improve performance. We have now developed an ion source with the following characteristics:

- 1) *Beam current.* Maximum achieved so far is $110\mu\text{A}$ (from samples originating as CO_2 or C_2H_2). Reliable generation of 30 to $60\mu\text{A}$ can be maintained until the sample is exhausted.
- 2) *Beam emittance.* 75 percent of the beam is contained within an emittance of $80\text{mm}^2 \cdot \text{mrad}^2 \cdot \text{MeV}$; while 90 percent is contained within $80\text{mm}^2 \cdot \text{mrad}^2 \cdot \text{MeV}$. The accelerator is designed with an acceptance of 100 to $120\text{mm}^2 \cdot \text{mrad}^2 \cdot \text{MeV}$.
- 3) *Efficiency.* The fraction of carbon in the source converted to C^- ions is measured to be in the region of 8 to 11 percent, for the type of samples we prepare under typical operating conditions.
- 4) *Fractionation.* This has been measured between $^{12}\text{C}^-$ and $^{13}\text{C}^-$, using ^{13}C enriched samples. The maximum fractionation cannot be measured to a better accuracy than about $\frac{1}{2}$ percent, but is, in any case, less than 1 percent for ^{13}C . The variation in fractionation can be measured to greater precision, and does not exceed 1 to 2 parts per mill as different portions of the ions source beam are selected. More accurate work must await accurate measurements on the complete system, but there are good grounds for believing that fractionation

in the source will not make a serious contribution to errors in the abundance measurement.

- 5) ***Amplitude stability.*** The ion beam current varies by ± 4 percent over a 5 to 10 minute period. For time scales of a second or less, the variation in amplitude is very much less than 1 percent and, generally, not more than 0.1 percent even at some preferred frequencies (such as mains frequency).
- 6) ***Memory and cross-contamination.*** Within a few seconds the C⁻ component of the source beam is reduced to beyond 10^{-6} when a non-C containing sample is used. All the indications are that cross-contamination is negligible for samples back to at least 60,000 years, but more precise measurements require the complete dating spectrometer.
- 7) ***Convenience.*** These figures have been achieved using samples in the form of graphite produced by cracking acetylene (or methane) on to hot wires, eg, Ta at 2000°C. We have shown that, to realize high beam currents of good emittance, the sample must be a good thermal conductor, and this rules out many possible sample types. Furthermore, we are doubtful that a source operating from gas, eg, CO₂ or CO, while more convenient, would show anything like the excellent efficiency, stability, and memory characteristics of the Cs-graphite sputter type. With the present source, the samples are located into the ion source in batches of 12 or so. Each sample is loaded as cracked onto the Ta substrate, on a thin strip about 1.5 mm wide and about 5mm long. The length of the strip can be scanned under the Cs beam while running, but only one side is used, with the other side available if required.

Sample preparation chemistry

We have started, but will not report here, to consider the chemistry involved in extracting material from archaeological samples that can be chemically purified to contain the relevant carbon for radiocarbon dating. A well-defined example would be the extraction of the characteristic amino acid hydroxy-proline from bone collagen. Here, we assume that a variety of more or less purified materials are available for dating, containing a carbon content of 1 to 5mg. More than this (except for very old samples) is unnecessary, while less will present increased handling problems. The main aim of the chemical work is to produce graphite at a reasonable yield without fractionation. The graphite, when formed, ideally should be spatially concentrated, so that it does not have to be scooped up for loading into the ion source. We have concentrated on the thermal cracking of gases, principally CO₂, CO, CH₄, and C₂H₂, using radio-frequency heating, focused CO₂ laser heating, and resistive wire heating. We have also examined other chemical routes, eg, the production of carbon from the reduction of CO by iron, but this produces too low a beam current. We obtain much higher yields from the resistive thermal cracking of C₂H₂ than from the other possibilities, and, for the relevant sample quantity, are able to deposit 50 to 60 percent of the carbon onto the Ta wire. While this might be improved

somewhat (the deposition of graphite is a complex and poorly understood process) we do not think that high yields, *ie*, > 90 percent, such that fractionation is thereby avoided, can be achieved. A further disadvantage is the formation of a small amount of TaC, which prevents samples smaller than 1mg or so from giving a useful graphite yield. The fractionation taking place at this stage is currently being studied. It appears that the process introduces a 1 to 1.5 percent fractionation of the ^{14}C (based on $\delta^{13}\text{C}$), but that it is fairly reproducible. Since the high energy mass-spectrometer continuously monitors the $\delta^{13}\text{C}$ value, with reference to a standard, this small degree of fractionation can be measured during the run. (A graphite standard would be required to measure the fractionation during sample preparation). The rest of the process, combustion to CO_2 , reduction to LiC and formation of C_2H_2 , is by the standard chemical route, but is on 1/1000 times the scale. We can prepare C_2H_2 with 85 to 90 percent yield and negligible fractionation on a 5mg scale. As is well known, the temperature of Li in the $\text{Li} + \text{CO}_2$ reaction is crucial for good yields, as is also the CO_2 pressure during reaction. With such small samples there is the possibility of sample cross-contamination, *eg*, during the attack of hot Li on its container, but we have not yet investigated this. The problem could be evaded by using a disposable liner, for example.

In summary, we believe we have developed a suitable method for routine operation for the conversion of 1 to 5mg carbon samples to graphite in a form that can be directly inserted in the ion source to give the performance listed above. The overall yield of this process is about 50 percent, and appears to introduce a small but measurable degree of fractionation, due to the cracking stage. The complete process is convenient to operate and should allow for a reasonably fast sample output. For very accurate work (better than $\frac{1}{2}$ percent measurements), or very small samples (less than 1mg) it may still be necessary to develop the process further, or perhaps sacrifice ion source operation by using chemically different material as the substrate.

Planned operation

The high energy mass spectrometer will have the following characteristics: from a sample of 1mg, 1 percent of the ^{14}C can be detected. This is based on the following figures:

Efficiency of conversion to graphite	50%
Source efficiency	10%
Transmission efficiency	75%
Charge state 3+ fraction	45%
Counting efficiency	100%

This gives 1.7 percent, but not all the carbon will be used in the source. Thus, a 1mg sample will yield statistics equivalent to date an error of ± 12 years on a modern sample, ± 120 years at 26,000 years, ± 1200 years at 53,000 years. At $30\mu\text{A}$ ion source current, the time taken for the consumption of such a sample is 4 hours. While for $\frac{1}{2}$ percent statistics on a

sample one-half to one life old, the time taken would be 25 minutes. This might well be doubled or more when comparison with a calibrated ion standard is made, but it does show that several samples per day could be dated, and that the time for sample preparation will be an important limitation.

While the accuracy of the method has been described in terms of the measurement of ^{14}C , other aspects are equally important. The possibility for chemical decontamination of the sample is a major help. Many samples submitted will enable multiple measurements to be made, perhaps after different chemical and mechanical treatments, so that the reliability of the date can be assessed. The new method for small samples clearly has great potential for tackling the problem of sample integrity.

REFERENCE

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