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Carbon-14: Direct Detection at Natural Concentrations

Abstract. The ^{14}C atoms naturally present in a piece of 19th-century wood have been detected directly by means of a tandem Van de Graaff accelerator used as a high-energy mass spectrometer. The ^{14}C ions were easily resolved from interfering ions with the use of a ΔE-E detector telescope (this telescope consists of a pair of detectors; one of them measures the specific ionization, ΔE, and the sum of the signals from both detectors gives the total energy for each ion, E_T). The technique offers a number of practical advantages.

In a recent article (*1*), Muller has discussed the advantages of directly measuring the concentration of ^{14}C atoms in a sample to be radiocarbon-dated, and has proposed a method for using a cyclotron as a high-energy mass spectrometer for such measurements. However, a tandem Van de Graaff accelerator appears to be a better choice for this purpose for a number of technical reasons. First, it has an external ion source easily adapted to quick sample changing. The ion source produces negative ions, and, since no stable or metastable negative nitrogen ions are known (*2*), this accelerator should automatically discriminate heavily against ^{14}N, the ion that would cause most difficulty in this measurement. The use of a ΔE-E energy telescope (*3*) as the ion detector will allow any small amounts of ^{14}N (and any other interfering ions) to be distinguished from the ^{14}C ions. Furthermore, the Van de Graaff accelerator is capable of accelerating all three carbon isotopes (^{12}C, ^{13}C, and ^{14}C) simultaneously. Given an appropriately designed analyzing magnet, these three isotopes may then be detected simultaneously, and the radiocarbon date may be obtained from the $^{14}C/^{12}C$ ratio. A correction for isotopic fractionation could be made based on the value of the $^{13}C/^{12}C$ ratio. Changes in the efficiency of the total system are only likely to take place at the ion source and acceleration stages. As these occur before the ions are magnetically separated, all three carbon isotopes will be affected equally, and the measured isotopic ratios will be independent of the system efficiency. In order to avoid making absolute efficiency measurements, it would be sufficient to compare the measured $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios of a sample of unknown age to that of a known radiocarbon standard, such as National Bureau of Standards oxalic acid.

To test the feasibility of this technique we conducted an experiment on the McMaster University model FN tandem Van de Graaff accelerator to determine whether ^{14}C could be measured at naturally occurring concentrations. We found that we could indeed detect the ^{14}C atoms in a piece of white spruce [*Picea glauca* (Moench) Voss] that spanned the decade 1880 to 1890 (*4*).

This wood was reduced to charcoal in a closed steel pipe. About 200 to 300 mg of the charcoal was placed directly in the cesium sputter source of the accelerator. Although carbon beams in excess of 100 μa have been obtained with such ion sources (*2*), only 0.5 μa were obtained from this charcoal sample. The beam was accelerated to the terminal where the negative ions were stripped of electrons by an oxygen gas stripper. At +7 Mv on the terminal the most favored charge state for carbon is 4+; the carbon ions thus emerged from the accelerator with an energy of 35 Mev.

A Faraday cup placed in the beam line a few meters past the analyzing magnet gave a reading of about 150 to 200 na when the beam optics and the field of the analyzing magnet were set appropriately for $^{12}C^{4+}$. When these settings were changed to values calculated for $^{13}C^{4+}$, a beam intensity of roughly 1 to 2 na was found, reflecting the relative natural abundances of ^{12}C and ^{13}C and indicating that accurate settings for a $^{14}C^{4+}$ beam could be calculated.

The normal system for stabilizing the accelerator voltage, measuring the current on the analyzing slits, could not be used for the ^{14}C measurement since there is insufficient beam current when ^{14}C is
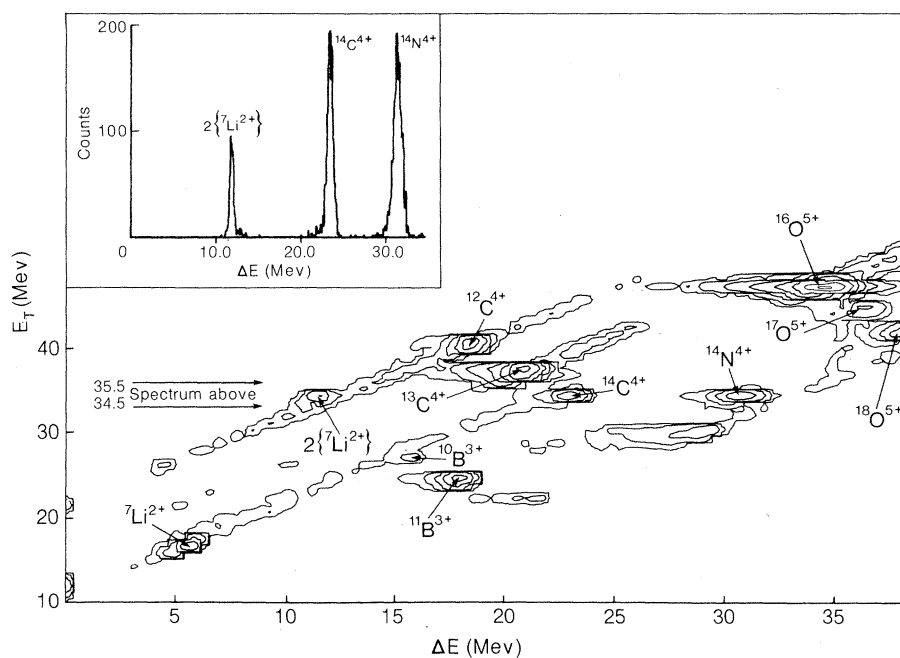

Fig. 1. A display of the number of ions detected in a piece of white spruce (1880 to 1890) (shown as contour lines at intervals 2, 8, 32, 128, 512, 2048, and 8196 counts) plotted versus the total energy (E_T) and the specific ionization signal (ΔE) of the ions. The inset shows the ΔE spectrum obtained from a count of those ions in the region E_T = 34.5 to 35.5 Mev. The isotopic species and charge states are identified. For example, the peaks labeled $^{7}Li^{2+}$ and $2\{^{7}Li^{2+}\}$ are due to acceleration of a Li_2^{-} molecule to the terminal, breakup of the molecule in the stripper, and subsequent detection of one or both of the lithium atoms.

accelerated. Instead, we used a system designed to measure and stabilize the terminal voltage directly. Unfortunately, this system was not designed for precise energy stabilization, and we observed, using the ^{12}C beam as a test case, that the beam energy was out of range of the analyzing magnet a major fraction of the time. Therefore, the integrated beam current based on the use of this direct stabilization system was only a fraction of what would have been obtained if the analyzing-slit stabilizer could have been used.

The ΔE-E detector telescope, used to identify the magnetically analyzed ions, consisted of two silicon surface-barrier transmission detectors of thicknesses 27 and 250 μm. These were mounted about 1 cm apart and operated in coincidence. (A third detector vetoed events in which ions passed through the first two detectors.) The first detector gave a measure of the specific ionization, ΔE, and the sum of the signals from both detectors gave the total energy, E_T, for each ion.

Figure 1 displays the number of detected ions, drawn as contour lines, plotted against ΔE and E_T. These data were collected over a 7-hour period. We established the identities of the peaks in Fig. 1, using the measured magnetic rigidity, total energy, and ΔE values. The analyzing magnet would allow only the ions with the specific charge states and masses shown in Fig. 1 to pass given their measured values. Comparison of the measured ΔE values for these ions with calculated values showed that all agreed within the expected experimental uncertainty except for those of the boron isotopes. It is not known whether this difference is due to error in the experiment or in the calculation.

The peak due to ^{14}C stands out clearly and contains about 800 counts. We would have expected about five times this number of counts from wood of this age if we had been able to use the precision energy stabilization system. However, the value is approximately that expected when the less precise direct stabilization system is used.

Unfortunately, we did not have an appropriate carbon sample of sufficient age to be able to measure the system background. However, one can estimate the background by examining the spectrum on all sides of the ^{14}C peak. Such an analysis predicts that less than 1 count in the ^{14}C peak is due to background. This is equivalent to the count rate expected for a sample age of 50,000 to 60,000 years. This result suggests that, with development, the technique will be capable of extending the age limit for ^{14}C dat-

ing much beyond that presently attainable.

The majority of the other ions detected result from the acceleration of molecular ions to the stripper with subsequent breakup into atomic ions of the appropriate mass-to-charge ratio. Since one can accurately identify these impurities, it should be possible to eliminate them at the ion source, although they are tolerable even at present levels. However, the energy of the ^{14}N peak suggests that this peak is due to acceleration of negative atomic ions from the source and not molecular ions (such as NH$^-$), although the energy resolution is not sufficient to permit us to be certain. If this is true, it may prove to be a hindrance to the development of high-sensitivity conventional mass spectrometers for radiocarbon dating.

Development of a routine dating system based on the use of the Van de Graaff accelerator should be straightforward. Designing the analyzing magnet such that ^{12}C, ^{13}C, and ^{14}C can be detected simultaneously will not only give an isotope ratio that is quite independent of the system efficiency but will also allow the beam energy to be precisely stabilized by use of the ^{12}C beam. Ion-

source development should yield ^{12}C beams of at least a few microamperes for sample sizes of tens of milligrams. This system is thus conceptually identical to existing isotope-ratio mass spectrometers, with the exception that the beam energy allows the use of a highly discriminatory ΔE-E telescope as a final detector.

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Radiocarbon Dating Using Electrostatic Accelerators: Negative Ions Provide the Key

Abstract. Mass spectrometric methods have long been suggested as ways of measuring ^{14}C/^{12}C ratios for carbon dating. One problem has been to distinguish between ^{14}N and ^{14}C. With negative ions and a tandem electrostatic accelerator, the ^{14}N background is virtually absent and fewer than three ^{14}C atoms in 10^{16} atoms of ^{12}C have been easily measured.

It has been recognized for some time (1) that one can achieve great improvements in the sensitivity of radioisotope dating by counting directly the number of radioactive atoms that are present in a sample rather than waiting for their decay and measuring the resultant radiation. More recently, Muller (2) discussed one possible way for making such direct measurements, using a cyclotron with a positive ion source as an extremely sensitive mass spectrometer. If such direct methods of measurement become possible for ^{14}C they could considerably increase the accuracy of ^{14}C dating and make possible new understanding of cosmic-ray fluctuations over many millennia.

In carbon from contemporary biological samples the ratio of ^{14}C to ^{12}C is approximately 1.2×10^{-12}. This ratio decreases by a factor of 2 for each 5730

years after the sample's death. If dating is to be done for samples having an age greater than 70,000 years, it is necessary to detect less than three atoms of ^{14}C in a sea of 10^{16} stable ^{12}C and ^{13}C atoms. The formidable problems expected in counting with such sensitivity, in the presence of ^{14}N contamination, have so far discouraged attempts to do it. The mass of the ^{14}N atom differs by only one part in 10^5 from that of the ^{14}C atom; thus in any mass spectroscopic method these atoms are virtually indistinguishable. Muller (2) suggested several ways of reducing the ^{14}N background, but all of these are difficult to apply in light of the fact that ^{14}N$^+$ is an almost inevitable contaminant from positive ion sources and can be expected with appreciable intensities ($\sim 10^{10}$ sec^{-1}).

Our earlier measurements (3) showed that the negative nitrogen ion is so fragile