

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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5. We thank D. G. Burke for his assistance and encouragement, J. McKay and the McMaster accelerator staff for their help, R. Toren for assistance with data analysis, and G. Brown for pointing out the usefulness of a negative ion source. Funding was supplied by Imperial Oil Limited and the National Research Council of Canada.

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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 $^{14}\text{C}/^{12}\text{C}$ 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 $^{14}\text{N}^+$ is an almost inevitable contaminant from positive ion sources and can be expected with appreciable intensities ($\sim 10^{10} \text{ sec}^{-1}$).

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

that the nitrogen contamination in ^{14}C measurements can be effectively eliminated by the use of negative ions. We report here that we have found it possible to detect the ^{14}C atoms directly at abundances about 5000 times lower than those from contemporary natural sources; in ^{14}C dating this would correspond to a source-to-background ratio of unity at about 70,000 years (4).

We analyzed, before acceleration, mass-14 particles produced in a negative ion sputter source (5), consisting mainly of $^{12}\text{CH}_2^-$ and $^{13}\text{CH}^-$, along with some $^{14}\text{C}^-$, using an inflection system of the University of Rochester Van de Graaff accelerator (6) capable of separating ions from the source whose masses differ by 4 percent. The selected particles were then accelerated to the tandem terminal and stripped either by a $10\ \mu\text{g}/\text{cm}^2$ carbon foil or by nitrogen gas. We maintained the terminal potential constant at 8 Mv (7) by using a generating voltmeter feedback circuit. This voltage was high enough to ensure that all molecules were dissociated in the stripper. After further acceleration, the particles were analyzed by a combination of two deflection magnets with their fields set to a value appropriate to $^{14}\text{C}^{4+}$ ions with an energy of 40.170 Mev (170 keV of acceleration was provided at the ion source).

In order to reduce the unwanted beams that still remain at this point, a stripper foil was introduced ahead of the magnetic spectrometer to charge-exchange the selected 4+ particles to 6+, thus requiring a field in the final magnetic spectrometer 4/6 of that for charge 4+. After this second stripping, we detected the particles using a position-sensitive E - ΔE counter in the focal plane of a magnetic spectrometer set at 0° to the incident beam axis. This counter, developed at the University of Rochester (8), consists of an ion chamber for the determination of total energy (E), two position-sensitive proportional counters which determine the angle and point of intersection of the particles with the focal plane, a ΔE plate (to measure the energy loss of the particles), and a final proportional counter at the rear of the chamber for rejecting events that are not stopped within the active volume of the counter. The various counter outputs, together with the terminal voltage, are digitized and fed to an on-line computer. This computer permits, for example, the following quantities to be displayed, recorded, and used in a variety of gating modes: (i) the magnetic rigidity of selected particles, (ii) the energy of selected particles, (iii) the atomic number (Z) and mass distributions (see Fig. 1),

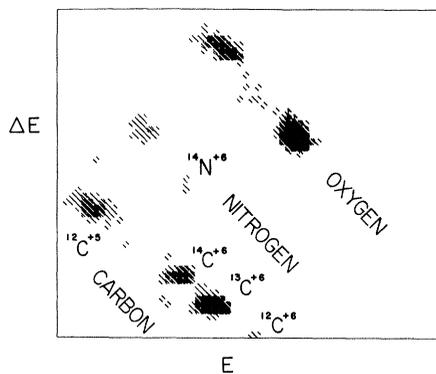


Fig. 1. The E - ΔE display from the detector system for a sample of contemporary charcoal. The particles are sorted according to their total energy (E) and their energy loss (ΔE) for a limited range of magnetic rigidity. Particles of the same atomic number Z lie on the same curve (hyperbola). Carbon, nitrogen, and oxygen are clearly delineated. The intensity of a group is displayed logarithmically according to the degree of blackness.

(iv) the energy loss (ΔE) of selected particles (see Fig. 2), and (v) terminal voltage variations. An on-line analysis program permits individual particles to be uniquely identified at rates up to 1000 per second.

We found that the very weak beam of $^{14}\text{C}^{6+}$ was contaminated by trace quantities of various other ions, which could be uniquely identified by the counter and which appear in Fig. 1 as hyperbolas corresponding to $Z = 6, 7,$ and 8 . A window on the $Z = 6$ hyperbola allows a display of counts versus ΔE (proportional to mass); this display is shown in Fig. 2 for

a petroleum-based graphite sample and for a sample of contemporary charcoal.

When the graphite sample (Fig. 2b) was used as a source of carbon ions in the ion source and when the source was adjusted to yield $10\ \mu\text{a}$ of $^{12}\text{C}^-$, $^{14}\text{C}^{6+}$ ions were readily observed at a counting rate of about $0.5\ \text{min}^{-1}$. No yield of $^{14}\text{C}^{6+}$ was expected from the petroleum-based graphite, and the observed counting rate is probably due to contamination of the graphite from contemporary carbon or from the slight enrichment of the ^{14}C in the hydrocarbons present in the ion source.

We found that $^{14}\text{C}^{6+}$ ions were readily observed from compressed contemporary charcoal (Fig. 2a) (9), and the peak counting rate was about $300\ \text{min}^{-1}$. However, the compressed charcoal was not as suitable a source of negative ions as the graphite, and only $1.2\ \mu\text{a}$ of $^{12}\text{C}^-$ was generated by the ion source during this measurement. It will clearly be possible to produce recent charcoal samples which have ^{12}C currents of 10 to $20\ \mu\text{a}$. Such currents would produce up to 3000 ^{14}C counts per minute.

The ratio of ^{14}C from these two sources (when corrected for the corresponding ^{12}C beams) was approximately 5000 to 1. This ratio corresponds to a concentration of less than three ^{14}C atoms in 10^{16} atoms of ^{12}C and establishes the date of the graphite sample as $\geq 70,000$ years. This age equals the maximum age that has ever been established by conventional radioactive decay

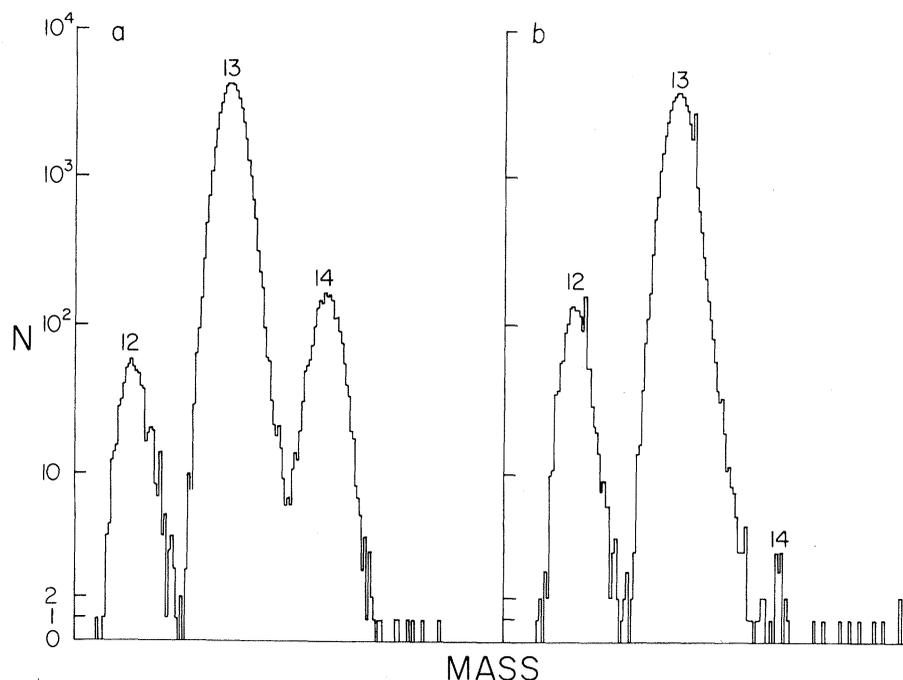


Fig. 2. The mass (ΔE) spectrum for events from a display similar to that shown in Fig. 1 where only the $Z = 6$ (carbon) charge 6+ events (N) are selected and plotted on the ΔE axis. The curve for contemporary hardwood charcoal is shown in (a) and that from petroleum-based graphite in (b).

counting techniques but uses sample sizes that are smaller by two orders of magnitude. The sample sizes used in the present work (1 g or less) can almost certainly be further reduced by a few orders of magnitude. The method will shortly be applied to the dating of carbon samples whose dates are well established by conventional methods.

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Carbon-14-Labeled Diethylstilbestrol Synthesis by the McMurry Method: Concurrent Formation of Hexestrol

Abstract. *Isotopically labeled diethylstilbestrol prepared from p-methoxypropiophenone by coupling with $\text{TiCl}_3\text{-LiAlH}_4$ contained approximately 50 percent hexestrol. Nonlabeled preparations and a subsequent labeled preparation had less than 2 percent hexestrol in them. Initial examinations for purity by gas-liquid chromatography, thin-layer chromatography, and isotope dilution did not show the presence of hexestrol. Specific ion monitoring of a gas chromatography-mass spectrometry determination revealed the presence of the diethylstilbestrol-hexestrol mixture.*

Uniformly labeled [^{14}C -diphenyl]diethylstilbestrol (^{14}C]DES) was prepared by the method of McMurry (1). [^{14}C -phenyl]*p*-Methoxypropiophenone was reacted with a reagent prepared from one equivalent of LiAlH_4 and two equivalents of TiCl_3 . The resulting methoxy derivative was demethylated with sodium hydroxide in ethylene glycol, and the product was purified by preparative thin-layer chromatography. Thin-layer chromatography on silica gel with a petroleum ether-ether system (4 : 6 by volume) indicated only *cis*- and *trans*-DES. The ratio of the *cis* to *trans* form was lower than expected for an equilibrium mixture; however, the rate of equilibration has been shown to vary with type of solvent, temperature, and the presence of other chemicals (2). Gas-liquid chromatography (GLC) of the trimethylsilyl derivative (4 percent OV-101; 80 to 100 mesh Gas-Chrom Q; column, 1.8 m by 4 mm; 150° to 250°C at 5° per minute) showed only *cis*- and *trans*-DES.

Our first hint of a purity problem came during isolation of the products after a degradation experiment in which DES (one part of the ^{14}C -labeled product under study with 173 parts of unlabeled DES) was allowed to stand for 3 weeks in 0.01N NaOH. A radioactive peak with relatively little mass was observed with a gas chromatographic system that simultaneously monitored mass (by flame ionization) and radioactivity. Because of this observation, we analyzed trimethylsilyl derivatives of the undiluted ^{14}C -labeled material by gas chromatography-mass spectrometry (GC-MS). As in earlier GLC analyses, two GLC peaks were obtained. The first (small) peak had the retention time of *cis*-DES and the second peak had the retention time of *trans*-DES. A plot of ion abundances for *m/e* (ratio of mass to charge) 412 (M^+ for DES) and *m/e* 207—one of the abundant fragment ions for pseudo DES (3)—showed that the first part of the second GLC peak resulted from a compound that yielded an ion of high abundance at *m/e* 207 and an ion of low abundance at *m/e* 412, whereas the last part of GLC

peak resulted from a compound that yielded an ion of low abundance at *m/e* 207 and an ion of high abundance at *m/e* 412. A mass spectrum taken during the first part of the second GLC peak was nearly identical to that of the trimethylsilyl derivative of hexestrol. Because of the uniform labeling of benzene rings, the increase in mass due to ^{14}C is distributed over a wide range of masses; therefore the ($\text{M} + 2$) peaks (414 for DES and 416 for hexestrol) and the ($\text{P} + 2$) peak for the 207 cleavage peak of hexestrol were not greatly increased.

With the evidence that the [^{14}C]DES preparation contained ^{14}C -labeled hexestrol and that a partial separation could be effected by GLC, we searched for better systems. The best GLC system found (3.5 percent OV-101; 100 to 120 mesh Gas-Chrom Q; column, 1.8 m by 2 mm; 180° to 230°C at 1° per minute) gave two partially resolved peaks with retention times of 15.7 and 16.2 minutes for hexestrol and DES, respectively. Areas under the curves suggested that approximately 60 percent of the material was hexestrol. Liquid chromatography [4.5 mm by 30 cm μ Porasil column, 5 to 10 μm (Waters Associates, Milford, Mass.), 5.0 percent tetrahydrofuran (THF) linearly programmed to 12.5 percent THF in hexane at a flow rate of 1.5 ml per minute over 15 minutes] gave complete separation of hexestrol from *trans*-DES (liquid scintillation counting of trapped peaks showed that 40 percent of the material was hexestrol).

An isotopic dilution determination made by recrystallization from benzene (10 μg of ^{14}C -labeled material and 400 mg of ^3H -labeled DES) gave a ratio of ^{14}C to ^3H that increased slightly with recrystallization, suggesting that the [^{14}C]DES was of higher purity than the ^3H -labeled DES. Recrystallization of 400 mg of hexestrol from benzene to which 5 μg of pure DES labeled with ^{14}C in the side chain had been added gave a nearly constant specific activity. Thus, during recrystallization from benzene, not only does DES serve as a carrier for hexestrol, but hexestrol also serves as a carrier