

An illustrated guide to measuring radiocarbon from archaeological samples

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Abstract

Radiocarbon dating has been central to the construction of archaeological chronologies for over 50 years. The archaeological, scientific and (increasingly) statistical methods for interpreting radiocarbon measurements to produce these chronologies have become ever more sophisticated. The accurate measurement of the radiocarbon content of an archaeological sample is, and always has been, fundamental to any interpretation. This article provides an overview of the different approaches adopted for measuring radiocarbon from archaeological samples by laboratories at the start of the 21st century.

Radiocarbon in nature

Radiocarbon (¹⁴C) is a naturally occurring isotope of carbon formed in the upper atmosphere by the interaction of cosmic radiation with nitrogen atoms (figure 1). It is unstable, with a half-life of 5730±40 years.

Once produced, radiocarbon quickly enters the terrestrial food chain by photosynthesis, and so the ¹⁴C content of all living organisms is in equilibrium with that of the contemporary atmosphere. When an organism dies it ceases to take up radiocarbon, and so over time the proportion of ¹⁴C in the dead organism decreases. By measuring the proportion that remains, the elapsed time since death can be estimated. The ratio of ¹⁴C in the material of unknown age to that in a modern standard is multiplied by the half-life to determine the age.

There are three physical characteristics of

radiocarbon that make it particularly difficult to measure.

First, the naturally occurring concentration of radiocarbon in living material is extremely low. The three isotopes of carbon occur in the proportions

$$^{12}\text{C} : ^{13}\text{C} : ^{14}\text{C} = 1 : 0.01 : 1.2 \times 10^{-12}.$$

This makes detecting a radiocarbon atom in a sample at the limit of detection (about 50 000 years old) equivalent to identifying a single specific human hair that might occur on the head of any of the human beings alive on earth today!

Second, the natural radioactivity of carbon is extremely low (226±1 Bq kg⁻¹ or 13.56 decays per minute per gram of carbon). This is within the range of natural background radiation on the Earth's surface, which makes distinguishing ¹⁴C radioactivity difficult.

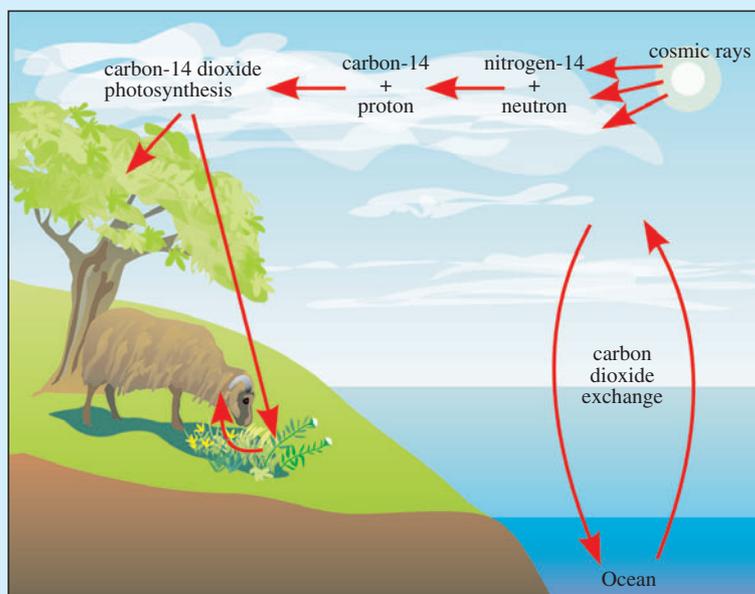
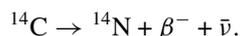


Figure 1. ^{14}C is formed in the upper atmosphere. Cosmic rays produce neutrons which collide with ^{14}N nuclei ($^{14}\text{N} + \text{n} \rightarrow ^{14}\text{C} + \text{p}$).

Third, the energy of the electrons emitted by the decay of radiocarbon is very low, and so they are difficult to detect. Radiocarbon disintegrates as follows:



where the reaction energy is distributed over the escaping electron (β^-) and the antineutrino ($\bar{\nu}$). The maximum energy of the β^- particle is as low as 156 keV. Further difficulties arise because the energies held by electrons produced by the decay of radiocarbon overlap with the energy spectrum produced by other decay products of contaminant radioisotopes, specifically radon and tritium (^{222}Rn and ^3H).

Other complications arise from the differential uptake of certain isotopes by physical and/or chemical processes. These processes, both in nature and in the laboratory, are dependent on mass. This is known as fractionation.

For example, in biological pathways lighter carbon isotopes are taken up preferentially, reducing the proportion of ^{14}C in a sample and thus its age. As the proportion of ^{13}C is also changed (and this is stable), the ratio of the stable carbon isotopes, ^{12}C and ^{13}C , in a sample can be used to estimate the fractionation of ^{14}C . This corrects a potential bias in the radiocarbon age.

Radiocarbon in archaeological samples

For accurate radiocarbon dating, only the ^{14}C that was part of the organism when it died should be measured. Therefore the first task is to remove any

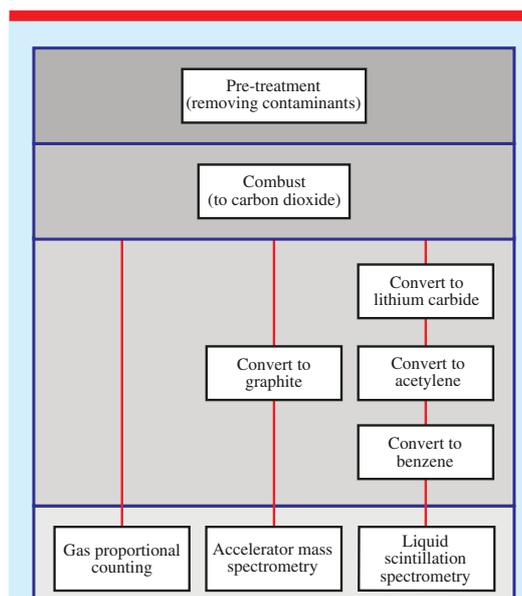
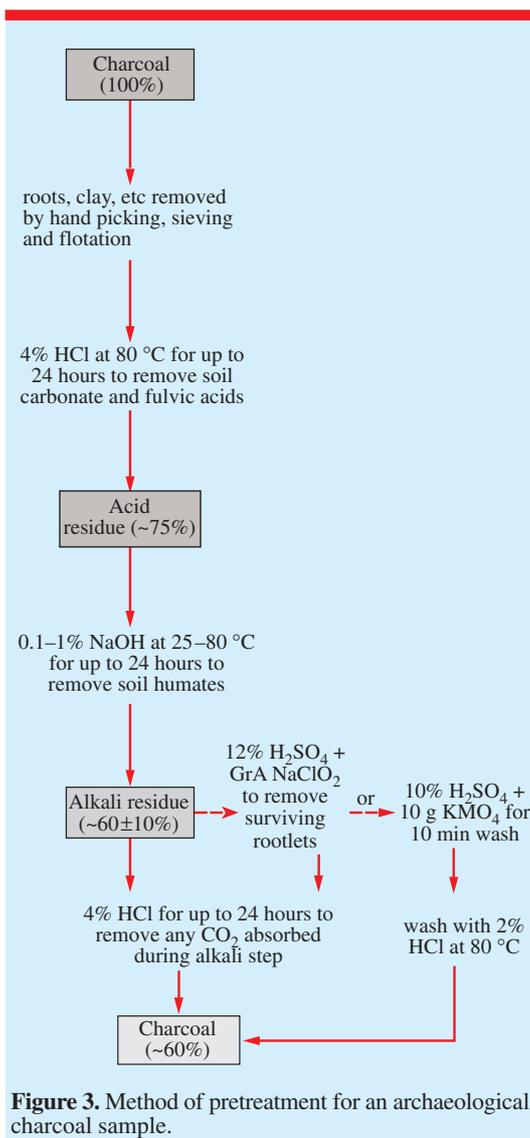


Figure 2. An overview of methods for measuring radiocarbon in archaeological samples.



foreign carbon that has entered the sample since that time (figure 2). Such contamination comes principally from the burial environment.

This is done by a mixture of physical and chemical means. A simplified outline of one of the pretreatment protocols is given in figure 3. The procedures also isolate a stable chemical fraction of a sample for dating (e.g. cellulose from wood).

Gas proportional counting

The next stage in dating is the combustion of the sample to produce CO₂ (figure 4). This is done in a stream of O₂ and N₂ typically over several



Figure 4. Sample combustion.

hours, to ensure complete combustion and avoid fractionation.

The resultant gas then undergoes a series of chemical processes to remove contaminating compounds and elements. A schematic diagram illustrating the complexity of this process is given in figure 5. The purity of the gas is critical (for example, O₂ must be kept well below a few parts per million). The CO₂ is then stored for a month to allow any ²²²Rn, which has a half-life of only a few days, to decay.

The radiocarbon content of the sample may now be measured. A diagram of the central portion of a gas proportional counter is shown in figure 6. The CO₂ is held under pressure in the central tube (typically at 2–3 atm), and a high voltage is introduced between the central wire and the counter wall. An ionizing event, such as a β⁻ particle produced by a ¹⁴C decay, creates an ionization trail and an avalanche of electrons. This avalanche is measured as an electrical pulse. Any impurities in the gas quench the multiplication of electrons, leading to some decay events being undetected.

For radiocarbon to be detectable, background counts must be minimized. There are two approaches for such shielding. Passive shielding is where a physical barrier absorbs ambient radiation and prevents it reaching the counter. Active shielding is where the background radiation is detected and eliminated from the sample counts.

At the University of Groningen, the gas proportional counters are surrounded by a passive shield of 40 mm of lead that is free of radioactive materials. Outside this is a ring of anticoincidence Geiger counters, which measure any background

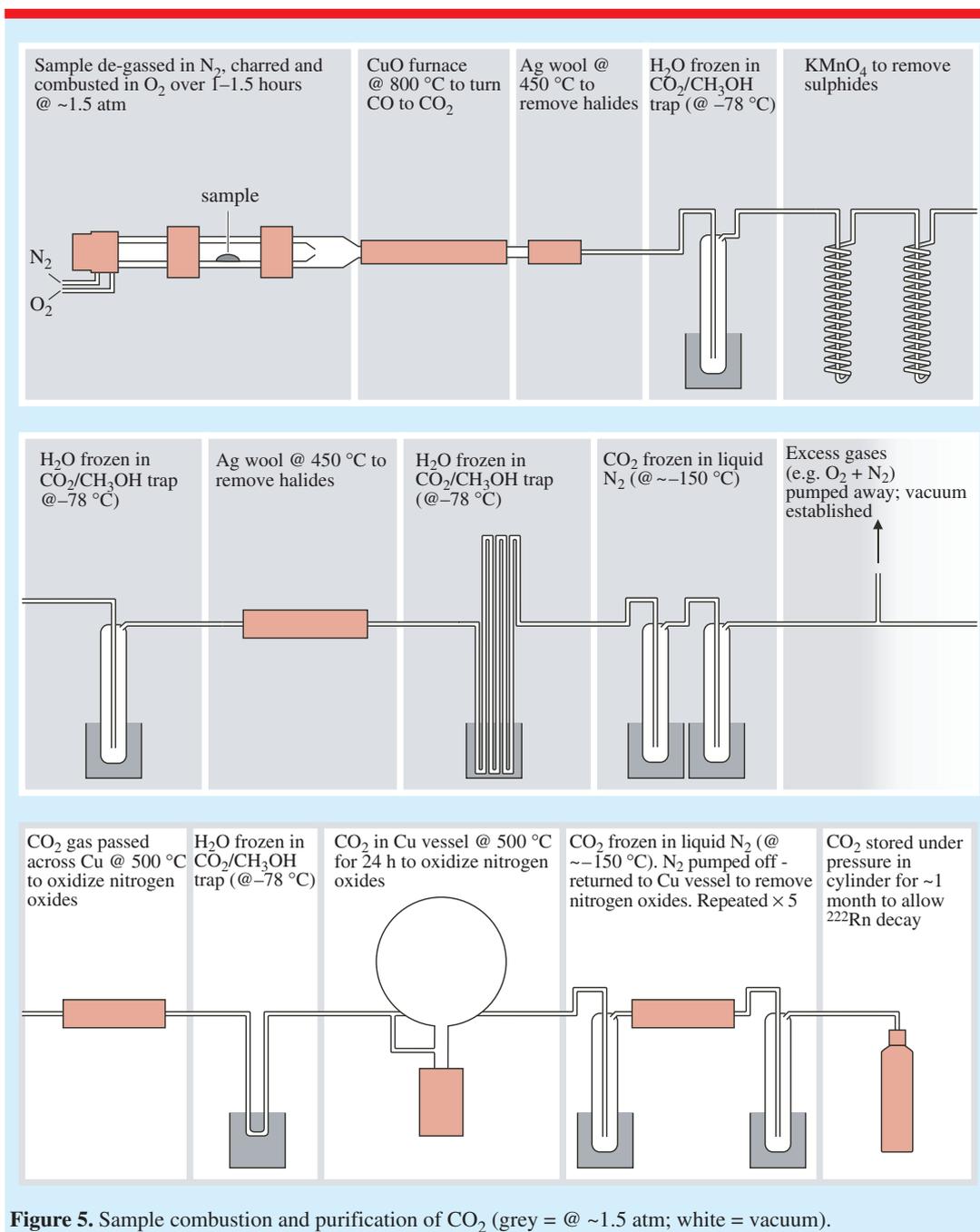


Figure 5. Sample combustion and purification of CO_2 (grey = @ ~ 1.5 atm; white = vacuum).

radiation that penetrates the shielding. If these counters measure a background pulse at the same time as the ^{14}C counters, then the count is rejected. Beyond this, 0.2 m of lead absorbs most of the γ radiation from cosmic rays. A 0.2 m layer of boron–paraffin absorbs ambient neutrons, which are moderated to thermal energy by the paraffin

and absorbed by the boron. Finally, another 0.2 m of lead and iron absorbs γ radiation (e.g. from ^{40}K in concrete) and the nucleon component of cosmic rays. Further passive shielding is provided by siting the counter below ground.

Typically samples are counted for 2–3 days.

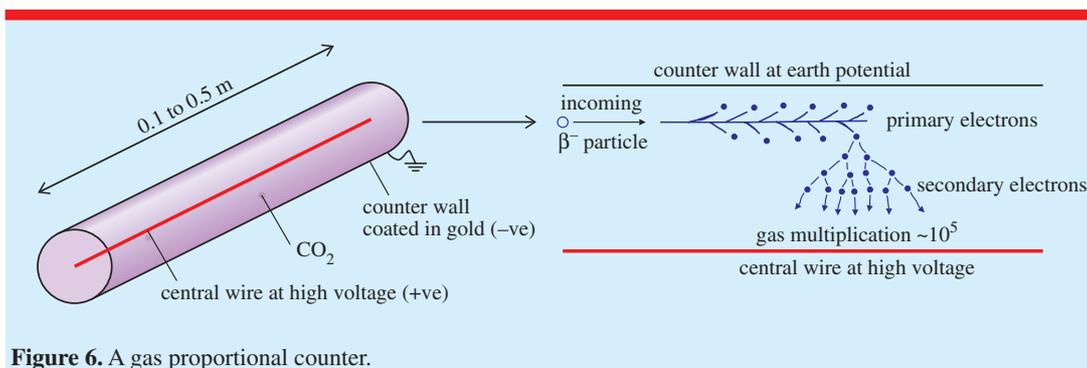
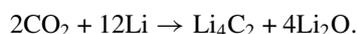


Figure 6. A gas proportional counter.

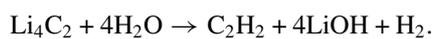
Liquid scintillation spectrometry

This method of radiocarbon dating also counts ^{14}C decay. The sample is pretreated and combusted to CO_2 as shown in figures 3 and 5. This is then converted to a carbon-rich liquid, benzene (C_6H_6).

A sequence of reactions is necessary. First the CO_2 reacts with molten lithium at $600\text{ }^\circ\text{C}$, according to the equation



Then ^{222}Rn -free water is added to the cooled vessel, producing the reaction



Water vapour is removed from the resultant acetylene (C_2H_2) in a cold trap ($\sim -20\text{ }^\circ\text{C}$). The C_2H_2 is then frozen and the H_2 pumped away (figure 7). It is then allowed to sublime slowly through beads coated firstly with sodium hydroxide (NaOH) and then orthophosphoric acid (H_3PO_4). The NaOH removes any remaining moisture and the H_3PO_4 removes ammonium compounds. The final step is the trimerization of the C_2H_2 to C_6H_6 , which is accomplished over a chromium oxide (CrO_3) catalyst at $40\text{ }^\circ\text{C}$. The benzene is collected and stored for at least three weeks to allow any ^{222}Rn to decay. Contaminant radon may be introduced from the catalyst.

When counting space is available, the sample is loaded into a low-potassium glass vial and an exact amount of scintillant added (butyl-PBD). This phosphoric compound dissolves in the benzene and produces a photon of light when a β^- particle is emitted.

Vials are placed in the liquid scintillation spectrometer (figure 8), along with known-activity and background standards. A schematic diagram



Figure 7. Purifying acetylene.



Figure 8. Loading samples in a counter.

of a counter is shown in figure 9. Photomultiplier tubes on either side of the sample detect the photons emitted by the ^{14}C decay. If both tubes register a pulse simultaneously and the energy of the combined pulse is within the expected range for radiocarbon, a count is recorded in a multichannel analyser.

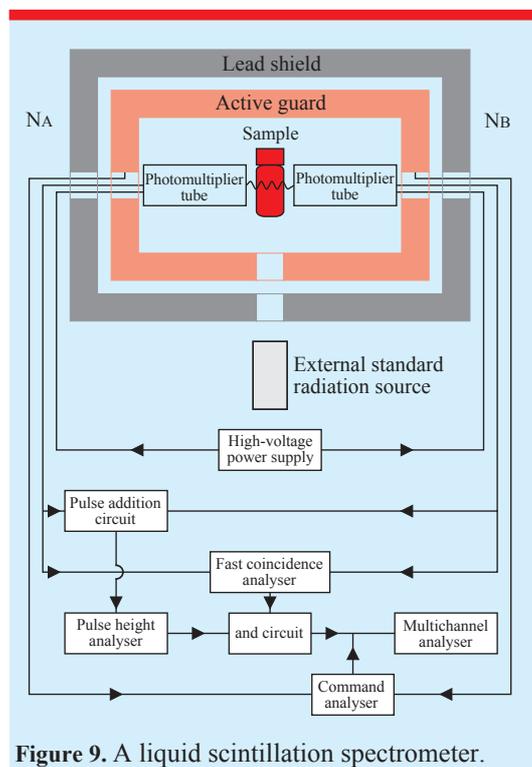


Figure 9. A liquid scintillation spectrometer.

Again, passive and active shielding is employed to distinguish between sample counts and background counts. The detector assembly is enclosed in 0.2 m of lead to absorb background radiation. Active shielding is provided by a mineral oil-based scintillator, known as the guard. The photons produced by background radiation events are also detected by two photomultiplier tubes within the guard. If these pulses are coincident with counts in the detector assembly, then the sample counts are discarded as they probably came from background radiation.

Two further checks are available to ensure the validity of the detected pulses. First, the energy spectrum of the pulse is measured to ensure that it has not shifted with respect to the spectra obtained from calibration standards. Second, the sample is irradiated by an external radiation source. This produces a flood of photons with a range of energies; if the benzene is pure then the end point of this energy distribution falls within a specific range.

Typically samples are counted for 1–3 months.

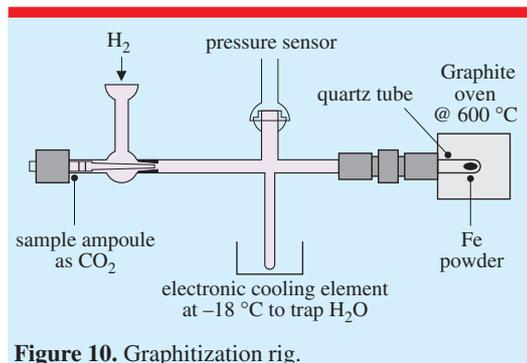


Figure 10. Graphitization rig.

Accelerator mass spectrometry

This method of radiocarbon measurement is fundamentally different, in that the ^{14}C is detected directly rather than through its decay. This means that dating of much smaller samples is possible, for example 1 g of bone rather than 200 g.

Pretreatment is outlined in figure 3. The sample is then placed in an automatic carbon–nitrogen analyser, which consists of a Cr_2O_3 flash combustion tube, and silver and copper furnaces to purify the resultant CO_2 .

The gas is then converted to graphite using an iron catalyst (figures 10 and 11), according to the equations



Figure 11. Graphitization.



Figure 12. Loading a target wheel.

The water produced by this reaction is removed to ensure a complete reduction to graphite. This is particularly important to avoid fractionation.

The graphite is then pressed into a target and

mounted on a wheel (figure 12) before it is loaded into the accelerator mass spectrometer (figure 13).

In the ion source a high current beam of caesium ions (Cs^+) is focused on the target. This liberates negatively charged target atoms, producing a ~ 36 keV beam of C^- ions. Targets are kept 10 mm away from each other to avoid cross-contamination, and moved during sputtering to avoid cratering, which causes fractionation. The negative ion beam is then focused by a lens into the recombinator.

Here a series of magnets remove non-carbon ions from the beam and separate the three carbon isotopes (^{12}C , ^{13}C and ^{14}C). The chopper wheel then physically blocks most of the ^{12}C , allowing a much reduced beam of carbon ions to be recombined for simultaneous injection into the accelerator.

In the tandem accelerator the C^- ions are accelerated to the terminal (at +2.5 MV; figure 14), then changed to C^{3+} ions by collision with Ar atoms in the gas stripper. These positive ions are accelerated to 10 MeV. A charge state of 3+ is chosen because the mass/charge ratio of $^{14}\text{C}^{3+}$ is truly unique, allowing its accurate separation in the high-energy mass spectrometer.

The first element of the high-energy mass spectrometer is a 110° bending magnet, separating the accelerated ^{12}C , ^{13}C and ^{14}C ions. The ^{12}C

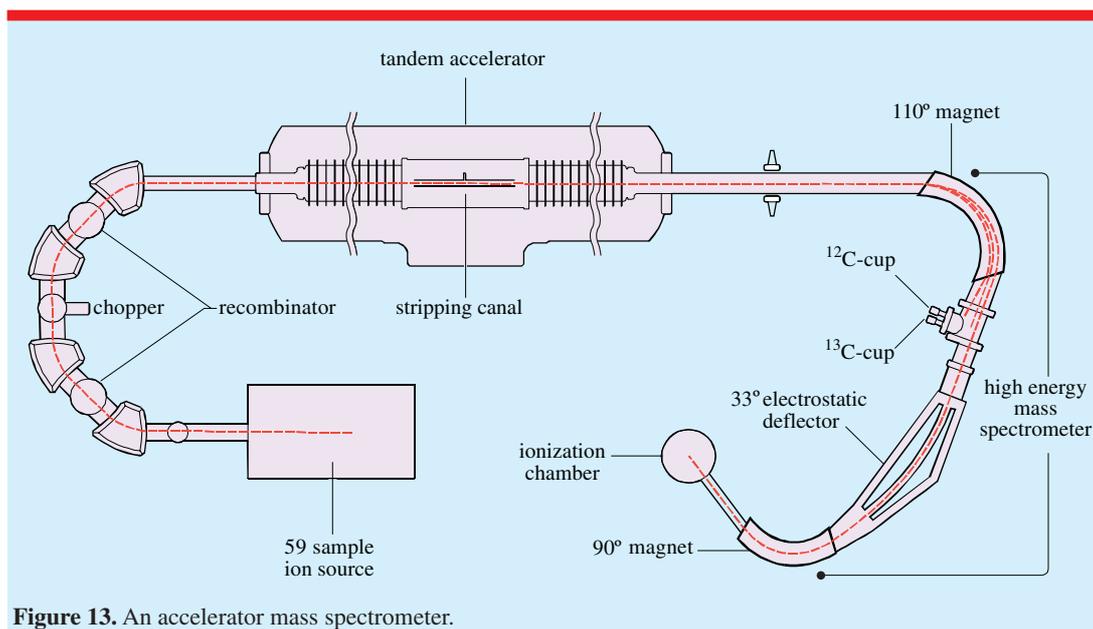


Figure 13. An accelerator mass spectrometer.



Figure 14. Repairing the 2.5 MV high-voltage generator.

and ^{13}C beams are measured in Faraday cups (typical currents ~ 250 nA). The $^{14}\text{C}^{3+}$ ions are further purified by a 33° electrostatic deflector and a 90° magnet. They are then measured in an isobutane-filled ionization chamber, isolated from the accelerator vacuum by a thin metal foil (density $\sim 250 \mu\text{g cm}^{-2}$).

Typically a sample is counted for one hour.

Producing a date

Once the radiocarbon activity of the sample has been measured, its radiocarbon age can be calculated using the equation

$$\begin{aligned} \text{Age } T &= -\frac{T_{1/2}}{\ln 2} \ln \left(\frac{{}^{14}A}{{}^{14}A_0} \right) \\ &= -8033 \ln \left(\frac{{}^{14}A}{{}^{14}A_0} \right) \text{ yr} \end{aligned}$$

where \ln is the natural logarithm (to base e), ${}^{14}A$ is the measured activity of the sample (in counts per minute per gram) and ${}^{14}A_0$ is the original ${}^{14}\text{C}$ activity as defined by the activity of the modern standard (by convention this equation uses a half-life of 5568 years, rather than the actual half-life of 5730 years).

For example, an antler recovered from the base of the main ring-ditch at Stonehenge was dated by liquid scintillation spectrometry at Queen's University, Belfast in 1994. This sample, UB-3788, has a measured activity (${}^{14}A$) which is 57.96% that of the standard (${}^{14}A_0$). These activities include corrections like those for fractionation, and so the radiocarbon age of the

sample is

$$\begin{aligned} -8033 \ln \left(\frac{{}^{14}A}{{}^{14}A_0} \right) &= -8033 \ln 0.5796 \\ &= 4381 \text{ BP yr.} \end{aligned}$$

Accounting for all the chemical and physical errors in measurement, this result is quoted as 4381 ± 18 BP.

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Further reading

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