

CHAPTER 10

Accelerator Mass Spectrometry

10.1 INTRODUCTION

Accelerator Mass Spectrometry (AMS) is an analytical technique that uses an ion accelerator as an ultrasensitive mass spectrometer to ultimately count individual atoms. AMS was first introduced in 1977 and constitutes a highly sensitive method for detecting very low concentrations of long-lived radioisotopes or stable isotopes in a wide range of samples.

AMS separates rare radioisotopes from stable ones and measures their relative ratio with high sensitivity and precision. It is commonly used in *radiocarbon dating* experiments, where carbon-based materials are converted to graphite, and the amount of ^{14}C they contain is measured. This provides a measure of the age of the item based on the half-life of the ^{14}C isotope of 5568 years. Meteorites from space, air trapped in Antarctic ice, and the Turin shroud are some of the sources of samples to which AMS has been applied. Other applications include studying radiolabelled tracers in biological systems.

In the AMS technique, the element of interest is chemically separated from the original sample and loaded as a target in the sputter ion source of the *tandem accelerator* (Figure 10.1). Samples are pulverised, treated with acid and alkali and freeze-dried. In the case of carbon-based compounds, the sample is converted to either graphite or carbon dioxide. After ionisation of the samples and the separation of ions using a magnet, negative ions containing the radioisotope of interest are accelerated through a potential of several million volts (MV). Negative ions are used to distinguish ^{14}C from ^{14}N since the latter does not form a negative ion. A gas such as sulphur hexafluoride is added to the accelerator to dissociate all molecular ions to an atomic form. At the end of this first acceleration stage these ions pass through a stripper. A stripper consists of a thin carbon foil or gas that strips electrons from ions and destroys any molecular isobars. In the case of carbon, any $^{12}\text{CH}_2^+$ and $^{13}\text{CH}^+$ ions are fragmented to leave only $^{14}\text{C}^+$ ions with a m/z of 14. These positive ions are further accelerated to energies of up

to several tens of MeV in the second stage of the tandem accelerator. Acceleration of the ions to high energies enables ions to be uniquely identified based on their total energy. Using a magnetic and electrostatic mass analyser, the ions are focused into a Faraday cup for ion detection. For carbon samples, the ratio of $^{14}\text{C}/^{13}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ is measured and compared to measurements made for standards of known ratios. It is possible to measure isotopic ratios down to $1:10^{-15}$, or low attomole levels.

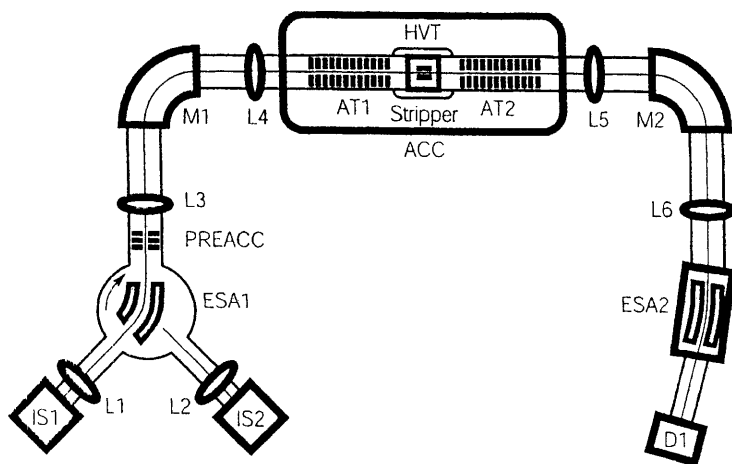


Figure 10.1 Schematic representation of a tandem accelerator mass spectrometer featuring dual ion sources, preaccelerator and tandem accelerator (ACC)

(Source: C. Tuniz, J.R. Bird, D. Fink and G.F. Herzog, *Accelerator Mass Spectrometry: Ultrasensitive Analysis for Global Science*, CRC Press, Boca Raton, 1998, Ch. 1, p. 42, Fig. 3.1)

AMS is unaffected by almost all background effects that limit conventional mass spectrometry measurements. Thus AMS is five to ten orders of magnitude more sensitive than a conventional mass spectrometry experiment. The amount of sample required for accelerator mass spectrometry is far less (typically a few mg) than that required for beta-particle decay counting, with around 1% of all the ^{14}C in a sample measured.

10.2 ION SOURCES

A typical AMS source consists of a heated reservoir of caesium powder, an ioniser that produces a Cs^+ beam focused at the sample, and an extraction electrode to accelerate and focus secondary negative ions

from the sample (Figure 10.2). Solid samples are deposited to a diameter of 1–2 mm in the centre of a cooled metal plate (usually cast of copper or aluminium) which acts as the cathode. The caesium ions are accelerated toward the cathode and on impact sputter or release particles from the surface. Such sputter sources efficiently produce negative ions for many elements and molecules depending on their electron affinity. The negative ions are injected into the accelerator where all molecular ions are dissociated and positive ions are formed.

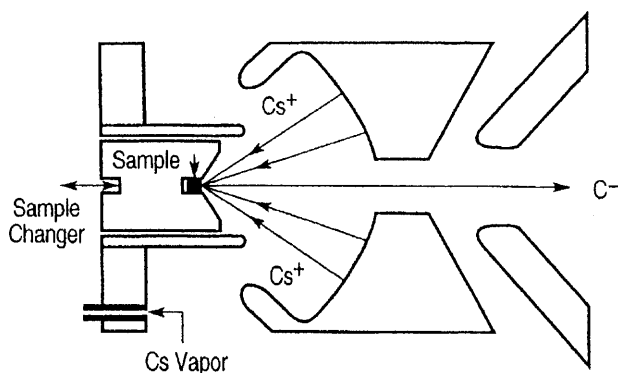


Figure 10.2 Schematic representation of a typical accelerator mass spectrometry ion source (Source: adapted from C. Tuniz, J.R. Bird, D. Fink and G.F. Herzog, *Accelerator Mass Spectrometry: Ultrasensitive Analysis for Global Science*, CRC Press, Boca Raton, 1998, Ch. 1, p. 43 – part (b), Fig. 3.2)

10.3 PERFORMANCE AND LIMITATIONS OF RADIOCARBON DATING

Many radioisotopes including ^3H , ^{14}C , ^{26}Al , ^{32}Si , ^{39}Ar and ^{81}Kr are produced in the atmosphere by cosmic rays through nuclear reactions. ^{14}C is produced by reactions between stable ^{14}N nuclei and neutrons in the upper atmosphere and is subsequently converted to carbon dioxide. This carbon dioxide is assimilated into plants, and through their consumption into animals. An equilibrium is maintained in the Earth's atmosphere, hydrosphere and biosphere through the continuous production of atmospheric ^{14}C . The stable isotopes of carbon (^{12}C and ^{13}C) constitute the majority of carbon on Earth (98.9% and 1.1% respectively). The level of ^{14}C on Earth, in contrast, is extremely low and has been measured to be about $10^{-10}\%$ of all carbon.

The measurement of ^{14}C is used in numerous applications of which radiocarbon dating is the best known. Radiocarbon dating involves measuring the ^{14}C in biological specimens or archaeological relics to

calculate their age. All living organisms or protected archaeological relics contain nearly the same proportion of radioactive carbon at the time of death or burial. The level of ^{14}C subsequently decreases by radioactive decay with a half-life of 5,568 years. By measuring the residual levels of ^{14}C in a sample, the age of the source material can be estimated.

The precision of radiocarbon dating measurements depends on a number of factors including the amounts of material available for analysis, contamination of the sample, reservoir effects, and variations in ^{14}C production. For specimens less than 5000 years of age, a minimum of about 50 μg of sample material is required for analysis. Optimal sample levels are of the order of a few mg to as much as a gram. At the lower levels, errors of the order of 1% in the age in years are typical.

Contamination is a major source of errors in AMS measurements particularly in older specimens. Bone carbonate, for example, is prone to the exchange of carbon from the environment particularly when buried in carbon-rich soils. The ^{14}C content in carbon dioxide trapped in polar ice cores can be measured providing it can be separated from that induced by radiation on the ice surface prior to it becoming buried. The so-called reservoir effect occurs when samples derive carbon not from the Earth's equilibrium but from local environments. These effects are apparent in plants found near volcanoes that release ^{14}C -depleted carbon dioxide and in deep sea aquatic systems.

10.4 APPLICATIONS OF RADIOCARBON DATING IN ARCHAEOLOGY AND COSMOLOGY

The shroud of Turin, an ancient cloth that many Christians believe was used to wrap Christ's body following his crucifixion, represents one of the most controversial radiocarbon dating experiments performed to date. The analysis was performed simultaneously at AMS facilities in Europe and the United States in 1988 from samples cut from the shroud in Turin, Italy. All three laboratories subdivided the samples, and subjected the pieces to different mechanical and chemical cleaning procedures to remove contaminants. The samples were further analysed microscopically to identify and remove any foreign material. All laboratories combusted the textile segments with copper and then converted the resulting CO_2 into graphite targets. Three to five separate measurements were made at each laboratory. The three laboratories in Arizona, Oxford and Zurich reported the age of the shroud at 641 ± 31 , 750 ± 30 and 676 ± 24 years respectively, far younger than is possible if the fabric had been used to wrap the body of Jesus Christ (Figure 10.3).

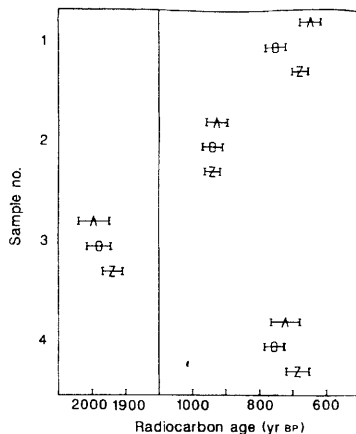


Figure 10.3 Mean radiocarbon dates, with a ± 1 standard deviation of the Shroud of Turin and control samples, as supplied by three laboratories (A, Arizona; O, Oxford; Z, Zurich). The age of the shroud is obtained as AD 1260–1390 with at least 95% confidence

(Source: P.E. Damon, D.J. Donahue, B.H. Gore, A.L. Hatheway, A.J.T. Jull, T.W. Linick, P.J. Sercel, L.J. Toolin, C.R. Bronk, E.T. Hall, R.E.M. Hedges, R. Housley, I.L. Law, C. Perry, G. Bonani, S. Trumbore, W. Woelfli, J.C. Ambers, S.G.E. Bowman, M.N. Leese and M.S. Tite, Radiocarbon Dating of the Shroud of Turin, *Nature*, 1989, **337**(6208), 611–615)

Radiocarbon dating measurements can also investigate when early civilisations first occupied land or cultivated crops. Controversy still surrounds the initial occupation of land in Europe, the Americas and Australia. The oldest known human occupation of territories in Australia has been dated at some 40,000 years ago, far before European settlement. Rock art of the indigenous Australian aboriginals uncovered in a series of excavations in far north Queensland has been dated at 26,000 years. Accelerator mass spectrometry has also been used to determine the age of maize cobs in Oaxaco in Mexico. Radiocarbon dating recorded the age of the maize, an ancient corn, at over 6,200 years old, making them the oldest known agricultural crops in the Americas.

The study of extraterrestrial materials from meteorite craters and rock are also of interest to scientists in order to establish that such materials are indeed extraterrestrial. Radiocarbon dating measurements can also be used to determine when such a meteorite collided with Earth and also its exposure to cosmic rays prior to collision in order to suggest its origin. The age of most specimens is evaluated based on ^{14}C and ^{41}Ca levels, the latter with a half-life of 130,000 years. Measurements of

^{41}Ca have the further advantage that its rate of production on Earth varies to a lesser degree than other isotopes.

10.5 BIOMEDICAL APPLICATIONS

^{14}C is used as a radioactive tracer in nuclear medicine both in medical research and for the testing of new pharmaceuticals on volunteers to follow metabolic processes and abnormalities. One method of following the metabolism of a ^{14}C -labelled drug compound, that has been ingested and metabolised, is to collect and analyse the end-product carbon dioxide exhaled. Clinically useful information is usually obtained from carbon dioxide exhaled a few hours after the administration of the drug, even if the time required for its complete metabolism is much longer. This approach has been used to study the long-term retention of ^{14}C -labelled triolein in fat by analysis of the patients' breath. There are, however, considerable errors in the estimates of the absorbed doses of ^{14}C -labelled pharmaceuticals largely due to the long half-life of ^{14}C .

The metabolism of calcium is also of interest in the study of bone diseases such as osteoporosis. An imbalance between the excretion and absorption of calcium from bone is responsible for osteoporosis and can only be partly counteracted by diets rich in calcium due to its absorption through the intestines at approximately 30%. The calcium isotopes ^{45}Ca and ^{47}Ca are usually employed as tracers since their half-lives are far shorter than ^{41}Ca (4.5 and 165 days respectively). In a bone absorption study in menopausal women, volunteers ingested 125 ng of radioactive calcium and their level of uptake was monitored by AMS measurements on their urine. The study's findings revealed a short-term rapid loss of calcium (by three orders of magnitude in 100 days) followed by a period of little loss (900 days).

Studies of the uptake of ^{26}Al from water sources have also been followed in rat brain by AMS in order to quantify the levels of environmental aluminium that enter the blood stream. The rate of passage of ^{26}Al from the blood to the brain is of interest in the study of Alzheimer's disease and other neurological disorders.

Other radioisotopes of importance in biomedical studies include ^{36}Cl and ^{129}I due to the abundance of these elements in insecticides and pesticides. Thus the levels of these compounds absorbed by humans can be measured as a function of exposure.

These studies demonstrate the far-reaching applications of accelerator mass spectrometry. They further illustrate the scope of experimentation and discovery possible a century after the founding of mass spectrometry.

FURTHER READING

- C. Tuniz, J.R. Bird, D. Fink and G.F. Herzog, *Accelerator Mass Spectrometry: Ultrasensitive Analysis for Global Science*, Boca Raton, Florida, CRC Press, 1998.
- H.E. Gove, *From Hiroshima to the Iceman: The Development and Applications of Accelerator Mass Spectrometry*, Institute of Physics, USA, 1998.