Sample Handling in Radiocarbon Dating by Accelerator with Special Reference to the Turin Shroud

Robert E. M. Hedges
Oxford University Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, 6 Keble Road, Oxford OX1 3OJ

Radiocarbon (^{14}C) is one of a handful of nuclides present on the earth at very low abundance (less than 10^{-12}) which are formed by cosmic rays and have half-lives in the 10^3–10^6 year range. Measurement of these nuclides is now possible by the recent technique of accelerator mass spectrometry (AMS), in which a negative ion beam of the nuclide is first generated, mass analysed and then injected into a tandem accelerator. The resulting multiply charged positive ion beam is further mass analysed, to the point where the final flux of particles into a detector is reduced to a level where ^{14}C (for example) can be positively identified. Usually an isotopic ratio measurement must be made to high accuracy (better than 1%). The main advantage of AMS is that samples more than 1000 times smaller than previously measurable by radioactive decay can be measured (*i.e.*, about 1 mg of carbon).

In radiocarbon dating, the steady-state abundance of ^{14}C (relative to ^{12}C) is kept spatially and temporally fairly constant throughout the biosphere by mixing processes (for example, dispersion as CO_2 and storage in the oceans). This level is sampled by living organisms, but then falls after death. For samples over 40 000 years old the ^{14}C level is less than 1% of the modern environmental level, so that contamination by recent carbon can be very serious.

Measurement by AMS implies, at present, producing samples in the form of graphite as targets to generate high intensity beams of C^-. However, the first step in processing a sample is to remove environmental contamination. The way in which this is done depends on the material being handled, but most of the current author's work is concerned with bone. In this case, the bone is superficially cleaned, and then decalcified in specially developed continuous-flow cells so that the insoluble collagen residue is retained. This is converted into gelatin, which is purified by ion-exchange and then subsequently hydrolysed to amino acids, which may be further purified. Most of the operations are done in batches, and the amount of transfer into different containers can be minimised. Different bones behave differently, and a flexible approach to treatment is necessary. It is mainly after the chemical purification is completed that laboratory contamination and handling become most important. The product is oxidised to CO_2, at present by heating with pure CuO, but we are developing at Oxford a method similar to that used in CHN analysers, where oxidation is in a stream of O_2, using tin capsules, and the gas is purified chromatographically. This still seems to produce a "blank" of about 1 μg, which is rather too high. The resultant CO_2 is then reduced to graphite (reduction to CO by Zn, and simultaneous catalytic conversion into graphite + CO_2 by Fe). We are in the process of building a source which can run from CO_2, which will avoid this last step. (However, the source itself can bring problems of cross-contamination.)

The work on the Turin Shroud involved most of the procedures indicated above. A full account is published in *Nature*, 1989, **337** (6208), 611–615. From our point of view, the most important result was that three laboratories could agree over four samples, when measured "blind," to an accuracy of better than 0.5%, although starting with textile samples which had had an unknown but potentially contaminating history.

Apart from work in archaeology, the Oxford University Radiocarbon Accelerator Unit undertakes other commercial work, and we would be interested in broadening our measurements on trace levels of ^{14}C. These would be appropriate where the total ^{14}C atoms available amount only to about 10^5–10^8.

Diamonds from Heaven and Hell

C. T. Pillinger
Planetary Sciences Unit, Department of Earth Sciences, The Open University, Milton Keynes MK7 6AA

The thought of diamond is able to provoke a different response from various people. Mechanical engineers, the electronics industry and the medical profession all use diamonds in different applications, and of course the jewellery trade puts a great many diamonds into (on to?) the hands of the general public. However, the common theme to everyone is the strength, resistance or persistence of the diamond; it is generally accepted as the symbol of eternity. To cosmochemists and geochemists the idea of eternity is a reality. Very fine grained diamonds fall from Heaven as a component of interstellar dust trapped in primitive meteorites. Likewise, diamond survived the molten hell of the deep Earth to carry to the surface a message of the geological processes which took place millions of years ago. Some of the most interesting secrets of diamond are recorded in the abundance of nitrogen (the most important trace element) and its isotopic composition, which taken together with the isotopic composition of the carbon constituting the bulk of the mineral provides fingerprint information related to the origin and provenance of diamond no matter where it comes from.

The difficulty in tapping this source of information has been in terms of reading it. Commercial mass spectrometers available up to 1983 to perform nitrogen isotope measurements needed about 4.5 μmol. Put another way, if diamond contains N at the 1000 p.p.m. level then 125 mg of the stone need to be destroyed to obtain the data; at the 20 p.p.m. level this rises to 6.25 g! To see this in perspective, it must be appreciated that 6.25 g represents about 5% of the world's biggest cut diamond, the Star of Africa. Consequently, until the development of instrumentation and techniques applicable to the investigation of N isotopes in diamond at the nanomole level, the scientific literature contained very little discussion of the subject.

One of the constraints in making measurements at high sensitivity is the problem that samples have been exposed to biological and atmospheric contamination sources which contain prolific amounts of nitrogen. A stepped extraction technique which distinguishes the nitrogen according to its volatility is able to resolve this question. In the case of meteorite studies, stepped combustion has been used to show that the diamonds contain nitrogen enriched by over 30% in