Enrichment: An Alternative Way to Extend Dating Range

Direct detection of carbon-14 is not the only approach that is being used to improve radiocarbon dating. Investigators are also seeking ways to increase the proportion of carbon-14 in the sample so that β decay can be detected more easily. The most advanced of these techniques, thermal diffusion isotopic enrichment, makes it possible to use conventional techniques for dating samples as old as 75,000 years.

Thermal diffusion enrichment of methane was, in fact, used by Willard Libby, now at the University of California at Los Angeles, when he first developed radiocarbon dating more than 30 years ago, but the technique fell by the wayside as better radioactive detectors were developed. Inspired by Libby's work, Jan Kistemaker and Adolf E. de Vries of the F.O.M. Institute for Mass Separation in Amsterdam, the Netherlands, in 1952 developed a technique for thermal enrichment of carbon monoxide. In 1956, Kistemaker and Hessel de Vries started a carbon-14 enrichment project and it continued in operation until 1967.

Several problems were encountered because of contamination, and few reliable results were obtained from the first device. The enrichment device was subsequently moved to the University of Groningen, where it was reconstructed by Pieter M. Grootes, now at the University of Washington. He succeeded in eliminating the contamination problems. A second device, constructed by Minze Stuiver, has been in operation at the University of Washington for 3 years. At least three laboratories in Europe are now constructing similar facilities for enrichment of methane.

The device at Groningen (Fig. 1) consists of nine upright tubes, each 6 meters in length. At the bottom of each tube is a collection vessel with a volume slightly more than 0.5 liter. The nine tubes are connected at the top to a series of storage containers with a total volume of 200 liters. A hot wire runs down the center of each tube and the outside of each is cooled by water. This creates a temperature gradient inside the tube; lighter molecules tend to accumulate slightly near the wire, while heavier molecules accumulate at the glass walls. Samples containing 60 to 120 grams of carbon can be enriched in the device.

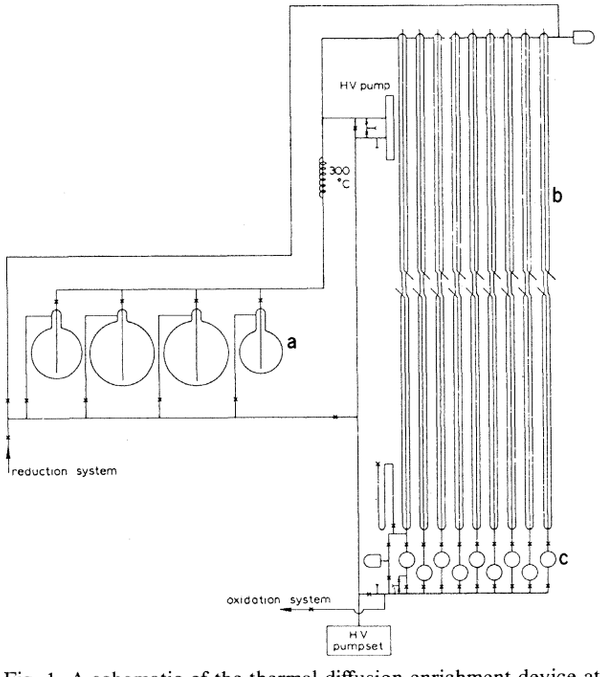

Fig. 1. A schematic of the thermal diffusion enrichment device at Groningen. *a*, Storage volume; *b*, thermal diffusion columns; and *c*, enriched sample volume. [Source: Pieter M. Grootes]

Because the tubes are in an upright position, convection currents carry the heavier molecules to the bottom containers and lighter molecules to the top. After the sample has been kept for 5 to 8 weeks in the device at Groningen, Grootes says, the amount of ^{14}CO in the bottom chambers is increased 10- to 14-fold. The Seattle device has a smaller storage volume and a larger collection volume; after a comparable period of time, the enrichment is 6- to 8-fold. The amount of enrichment is monitored by measuring the enrichment of naturally occurring $^{12}C^{18}O$—which has the same molecular weight as $^{14}C^{16}O$, but is more abundant—in a mass spectrometer.

Grootes has used the device to date samples of peat, lignite, moss, and wood obtained from glacial deposits in northwest Europe. He determined the dates of samples as old as 72,300 years and found that the dates correlated well with those obtained in more indirect geological studies. In a similar fashion, Stuiver, Calvin J. Heusser, and In Che Yang of the University of Washington have used enrichment to date samples from glacial deposits in the Great Lakes and the Pacific Northwest regions of the United States. They have used their results to develop a time scale for the recent glacial history of the two regions and have reported the oldest date—74,700 years for the St. Pierre, Canada, interstade—so far determined by carbon-14 dating.

Alternate Route to Enrichment

An alternative route to enrichment is laser photochemistry. In 1975, Bradley Moore and his associates at the University of California at Berkeley demonstrated that laser photolysis of $^{13}CH_2O$ could be used to increase the concentration of carbon-12 in a mixture of $^{13}CH_2O$ and $^{12}CH_2O$ (when the sample is struck by light of a precise wavelength, only $^{13}CH_2O$ is broken down into smaller components that can be readily separated from the remaining $^{12}CH_2O$). Using the same principle, but subjecting $^{12}CH_2O$ to photolysis, Robert Hedges of Oxford University has demonstrated that it is possible to enrich the concentration of carbon-14 in a sample by a factor of 100, the equivalent of reducing the age of the sample by 38,000 years. With a suitably designed system, he argues, it should be possible to enrich samples 400-fold.

With the use of a high-powered krypton-fluorine laser and dye amplifiers, Hedges says, it should be possible to enrich samples as large as half a gram within an hour. He thinks it unlikely that enough enriched material could be produced for β counting, but the material could be readily used in an accelerator mass spectrometer. Hedges, E. T. Hall, David Sinclair, and their colleagues at Oxford University have, in fact, been performing design experiments on the tandem Van de Graaff accelerator at Oxford and are now beginning construction of a dedicated facility. One of the goals of the new machine will be to prove the utility of laser enrichment.—T.H.M.