Reports

Carbon-14 Dating: A Comparison of Beta and Ion Counting

Abstract. *Accelerator ion counting compares favorably with conventional beta counting. The major advantage of ion counting is that milligram samples can be analyzed. When sample size is not limiting, ion counting complements beta counting for the more routine carbon-14 determinations. Further development is needed before ion counting can achieve the same high precision as beta counting for large samples (± 2 per mil). A solution to the background variability has to be found before ion counting can be used to date samples back to the 75,000-year limit of beta counting.*

Much information has been gained from ^{14}C research since the first measurements of natural ^{14}C activities were made in 1946 (*1*). Carbon-14 activities are now measured in more than 100 laboratories (*2*), and few other techniques developed since World War II have contributed to such a wide variety of academic disciplines. Any improvement in technique, such as the recently developed mass separation method (*3-5*), is of major importance for research in many fields. If the isotopic species under consideration is sufficiently abundant, mass separation is preferable to radioactive decay counting. For instance, routine mass spectrometer determinations of ^{13}C/^{12}C ratios can be made with a precision of at least ± 0.02 per mil. Decay counting cannot match this precision for radioactive materials.

The major obstacle in applying mass separation to ^{14}C dating has been low ^{14}C content. A sample formed in equilibrium with atmospheric CO_2 during the 19th century contains only 1.4×10^{-12} g of ^{14}C per gram of carbon, compared to 0.01 and 0.99 g, respectively, of the stable isotopes ^{13}C and ^{12}C. For a sample 57,000 years old, the quantity of ^{14}C is 1000 times less, or 1.4×10^{-15} g. When one is separating according to mass, these minute quantities of ^{14}C have to be distinguished from the much more abundant ^{14}N or, in the case of $^{14}CO_2$, from $^{12}C^{16}O^{18}O$. The ^{14}C also should not overlap ^{12}C or ^{13}C, which are at least 10^{12} and 10^{10} times more abundant, respectively.

These separation problems were finally surmounted by using negative ion techniques and nuclear accelerators (*3-5*). With the new Van de Graaff mass separation technique, ions are produced from the sample in an ion source, accelerated, and subsequently detected. The ^{14}N problem is solved by using negative source ions, since metastable negative nitrogen ions are so fragile that they do not survive acceleration in the Van de Graaff tandem accelerator (*6*). Molecular fragments of mass 14 are broken down to single atoms in a stripper foil, where negative ^{14}C ions lose outer electrons and are further accelerated as $^{14}C^{3+}$ ions. Magnetic separation of the nuclear ions is used together with ion acceleration to high energies so that high-resolution discrimination of energy versus energy loss can be used in the detector, where the ^{14}C ions are counted. Cyclotron techniques have also been applied. Further technical details are given in the original articles (*3-8*). The mass separation method can be characterized as ion counting, the conventional technique as beta counting. An advantage of beta counting is the use of simple experimental devices such as proportional counters or scintillation detectors. All ^{14}C measurements were made in this manner between 1946 and 1977. Thus ^{14}C was detected indirectly by counting the number of electrons emitted during the disintegration of the ^{14}C atoms.

Beta counting, however, has a serious drawback because the rate of ^{14}C disintegration is very low. Each day the fraction of ^{14}C decaying equals only 3.3×10^{-7} of the amount of ^{14}C present. After a full 3 days of counting only one millionth of the amount of ^{14}C present in the counter is actually counted. The amount of ^{14}C that can potentially be used for ion counting is 10^6 times larger than the amount of ^{14}C actually detected through beta decay.

Several aspects have to be considered when comparing ion and beta counting. They include sample size, the accuracy to be obtained, the economics of the laboratory analysis, and background. The samples routinely analyzed at the Quaternary Isotope Laboratory for beta counting contain, after pretreatment, approximately 0.5 to 7 g of carbon. Smaller sample sizes, down to 100 mg of carbon or less, have been used for special applications such as ice dating (*9*). Samples containing up to 120 g of carbon have been used for dating back to 75,000 years by a combination of isotope enrichment with ^{14}C counting (*10, 11*).

The sample size needed for ^{14}C ion counting is a minuscule 10 mg of carbon or less. (With a commercial mass spectrometer ^{13}C/^{12}C isotope ratio measurements can be made, for instance, on a sample containing 20 μg of carbon.) Samples much larger than 10 mg are generally not used because the basic ion source design limits sample size. The accelerated ^{14}C ions are transmitted through the analyzer tube without much loss. Bennett *et al.* (*5*) reported a 10 to 80 percent transmission efficiency, depending on conditions. The ion sources employed successfully with Van de Graaff mass separation have been of the solid carbon sputter variety. The reported $^{12}C^-$ ion currents generated from a solid carbon source are 1 to 7 μA for samples in the size range 3 to 15 mg (*5*). Such currents are generated by only 4.4×10^{-4} to 3.1×10^{-3} mg of $^{12}C^-$ per hour. Since the sputter cone contains up to 15 mg of carbon, the amount of sample introduced is substantially larger than the amount of material actually converted to ions. With improvements of ion source design one can visualize the dating of 10^{-2} mg of carbon.

A simple direct comparison of both methods can be made by considering the amount of ^{14}C actually counted, either as decaying atoms for beta counting or as ions for mass separation. More accurate results are obtained when larger amounts of ^{14}C are measured because the relative error in the number of counts, N, decreases as N increases.

Two grams of carbon is a fairly typical sample size for beta counting. Since only one millionth of the ^{14}C present decays in 3 days, the weight of ^{14}C atoms that decay in a 2-g 19th-century sample that contains 1.4×10^{-12} g of ^{14}C per gram of carbon is $2 \times 1.4 \times 10^{-12} \times 10^{-6} = 2.8 \times 10^{-18}$ g. This is also the actual amount of ^{14}C counted because the efficiency of proportional counters is close to 100 percent. The number of counts over the 3-day interval that corresponds with this amount of ^{14}C is 120,000, giving a ± 0.3 percent standard deviation in the sample count.

In the mass separation method, the

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amount of carbon ionized and accelerated is 3.1×10^{-6} g for 1 hour of accelerator operation when the source ion current is 7 μA. The amount of ^{14}C in the source ion current for 19th-century materials is $1.4 \times 10^{-12} \times 3.1 \times 10^{-6} = 4.3 \times 10^{-18}$ g. For a fairly high ion beam transmission efficiency of 70 percent in the accelerator and a $^{14}C^{3+}$ yield of one-third through the stripper foil, the amount of ^{14}C actually counted in 3 hours in the detector is $0.7 \times 0.33 \times 3 \times 4.3 \times 10^{-18} = 3.0 \times 10^{-18}$ g.

For both cases the actual amounts of ^{14}C counted are nearly equal under the specific conditions stated. The following points are noted. The amount of ^{14}C available for analysis in ion counting is 1 million times the amount available in 3 days of beta counting. The typical sample used for ion counting (10 mg) is 200 times smaller than the sample used for beta counting (2 g); this leaves 5000 times more ^{14}C available for analysis in the direct method. However, the inefficiency of the ion source used to generate the ion current offsets the latter advantage. As a result, about the same number of counts are registered in the detector in both methods (for 3 hours of accelerator time versus 3 days of beta counting).

In Fig. 1 both methods are compared under more general operating conditions. The lines drawn represent conditions under which ion and beta counting give the same number of counts in the detector. Thus, for instance, a 3-hour ion count with a source current of 10 μA produces the same number of ^{14}C ions in the detector as a 1- or 4-day beta count with 8.8 or 2.2 g of sample, respectively.

A 70 percent accelerator ion beam transmission efficiency was assumed in the calculations for Fig. 1. However, the ^{14}C measurements reported by Bennett *et al.* (*5*) were made with a 25 percent transmission efficiency. Under those conditions the horizontal scale in Fig. 1 has to be multiplied by 2.8. The lower efficiency makes ion counting less competitive with beta counting. Although source $^{12}C^-$ ion currents of 7 μA or less have been reported for routine samples (*5*), improvements to 10 μA are certainly possible. In fact, the maximum ion current in a single experiment not related to ^{14}C dating was 100 μA (*4*). Provided that 10-μA ion currents and 70 percent transmission efficiencies can be routinely obtained, more ^{14}C can be counted in 1 hour of ion counting than in nearly 3 days of beta counting for samples smaller than 1 g of carbon (Fig. 1).

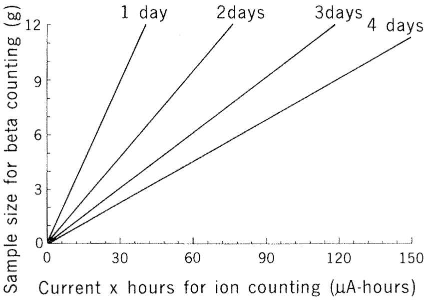

Fig. 1. Lines for which both ion and beta counting give the same results when equipment stability is not a limiting factor. A transmission efficiency of 70 percent and a one-third yield of $^{14}C^{3+}$ ions through the stripper foil are assumed for ion counting (see text). The sample size for ion counting is approximately 10 mg. Duration of beta counting is given in days.

Beta counting utilizes samples in the range 7 to 20 g for high-precision work. For a 7-g carbon sample and 4 days of counting, the overall accuracy obtained in the Quaternary Isotope Laboratory is better than 2 per mil when the inaccuracies in standard and sample counts are taken into account. Such an accuracy can potentially be achieved with ion counting only when the accelerator time is increased to several hours (90 μA-hours in Fig. 1).

The cost of commercial ^{14}C sample preparation and beta counting is approximately $150 for up to 2 days of counting. For high-precision work (±2 per mil or less) the counting time may be up to 4 days, the samples are larger and require more treatment time, and a beta determination may cost $300. This includes the depreciation on investment in equipment, the cost of the technicians' time to remove contaminants through sample pretreatment, and the cost of combustion, purification of the CO_2 derived, and possibly conversion to another counting gas or liquid.

The first step, removal of contaminants, is also necessary for samples used for ion counting. Present ion source technology (*3, 5*) requires reduction of the sample to pure carbon and preparation of the ion source cone. The costs of these steps are estimated as $60 per sample. The operating cost for the accelerator is estimated as $150 per hour, not including depreciation. It would seem that an accelerator run of 1 hour yielding a routine ^{14}C date (±100 years) is at least as expensive as a high-precision 4-day beta measurement (±30 years for a 5000-year-old sample).

For age determinations on old samples, background and stability are extremely important. Large counters are used for beta counting with such samples. The maximum possible age that can be determined in this manner at the Quaternary Isotope Laboratory, using a counter with a background of 1.5 counts per minute, is 60,000 years for a 7-g sample in 4 days of counting (*12*); samples of zero age register nearly 100 counts per minute with this counter. The background rate over an interval of several months does not fluctuate more than the standard deviation expected from Poisson counting statistics ($N^{1/2}$ in N counts) (*13*).

Very low backgrounds have also been reported for ion counting (*3-5*); however, they do not appear to follow a Poisson counting distribution. Variable background changes equivalent to an age determination of 40,000 to 70,000 years have been reported (*5*). These background problems may be related to ^{14}C adsorbed on the solid carbon ion source cone or to a memory effect from previous samples with higher ^{14}C activities. This problem has to be solved for ion counting before its projected use for ^{14}C dating back to 100,000 years (*8*) can be taken seriously. Even if such an age range is feasible, our experience shows that it is extremely difficult to avoid laboratory contamination in the 75,000-year range. An addition of modern material of only 0.1 per mil changes a 75,000-year age to somewhat less than 70,000 years. A nuclear accelerator facility is not an ideal environment for sample handling and preparation because man-made ^{14}C increases the risk of sample contamination.

Because of the stability of the equipment used for beta counting, it is possible to determine ^{14}C ratios for large young samples with an accuracy of ±2 per mil (±16 years) or less. For ion counting, such levels of operating stability have not yet been reached. The ages determined so far (*5*) have standard errors of about 400 years (±5 percent) for 5000-year-old samples. Routine dating of samples of Holocene age with age errors of ±100 years certainly appears within the reach of ion counting. Beta counting, combined with thermal ^{14}C enrichment, has been used to date samples back to 75,000 years (*10, 11*). Ion counting has the same potential for much smaller samples, provided background stability can be improved. Isotope enrichment will be useful for ion counting because much higher enrichment factors can be obtained for the smaller samples needed.

The superb advantage of ion counting is the small sample size. Beta counting cannot compete with ion counting for samples smaller than 1 g of carbon because the number of beta counts becomes too small. The expense of collecting samples also depends on sample size. At the Quaternary Isotope Laboratory the ^{14}C activity of ocean water samples is being measured (*14*) with an accuracy of ±4 per mil. To obtain such accuracy the CO_2 has to be stripped from 200-liter seawater samples. Large Gerard barrels are used to collect the samples, and only a few large samples can be collected on each cast. If the accuracy of ion counting could be improved to ±4 per mil, much smaller samples could be used. Large numbers of 1-liter samples could be collected in a single cast and shipboard time would be reduced.

Many problems that elude beta counting can be studied with ion counting. Amino acid racemization dating can be internally checked by determining the ^{14}C age of single amino acids. Carbon-14 studies of the CO cycle (oceanic versus anthropogenic CO) are within reach. Fraudulent oil paintings can be detected more easily because it is not necessary to combust appreciable portions of the painting. Cave paintings in which organic materials such as blood were used can be dated directly with ion counting. It is no longer necessary to use huge ice samples, up to 5 tons for dating; sample amounts can be reduced to 100 kg. Thus, although beta counting will still be used in the future, ion counting will tremendously enlarge the range of applications of ^{14}C analyses.

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Strain in Southern California: Measured Uniaxial North-South Regional Contraction

Abstract. *The plate tectonics model of the Pacific moving northwest relative to North America implies that the regional strain in California should be simple shear across a vertical plane striking N45°W or equivalently equal parts of north-south contraction and east-west extension. Measurements of the strain accumulation at seven separate sites in southern California in the interval 1972 through 1978 indicate a remarkably consistent uniaxial north-south contraction of about 0.3 part per million per year; the expected east-west extension is absent. It is not clear whether the period from 1972 through 1978 is anomalous or whether the secular strain in southern California is indeed a uniaxial north-south contraction.*

As part of the earthquake studies program of the U.S. Geological Survey, seven trilateration networks along the major faults in southern California (Fig. 1) have been surveyed several times during the period from 1972 through 1978. In each survey the distances between geodetic monuments within the network are determined. The distances are measured with a Geodolite, a precise electrooptical distance-measuring instrument, and the refractivity corrections are calculated from temperature and humidity profiles determined from aircraft-mounted sensors flown along the line of sight at the time of ranging (*1*). The errors in distance determination are described by a normal distribution with a standard deviation ranging from about 3 mm at a few kilometers to about 7 mm at 30 km (*1*).

To calculate the average strain rate tensor for each network, it is assumed that the strain rate is uniform in space over the breadth of the network and in time over the interval from 1972 through 1978. The changes of length of the individual lines then yield a large number of strain rates at various orientations from which the three components of the surface strain rate tensor ($\dot{\epsilon}_{11}$, $\dot{\epsilon}_{12}$, and $\dot{\epsilon}_{22}$ in a coordinate system with the 1 axis directed east and the 2 axis directed north) can easily be computed. Because a large number of lines (about 30 for each network) are used to calculate just three strain rate components, reliable estimates of both the strain rate components and their standard deviations may be made. The standard deviations reflect not only the observational uncertainties but also the departures from the assumed uniformity of strain accumulation in both space and time.

The tensor strain rates with standard deviations for the seven networks are shown in Table 1, and the principal strain rates are shown in Fig. 1. Each of the networks may be described adequately

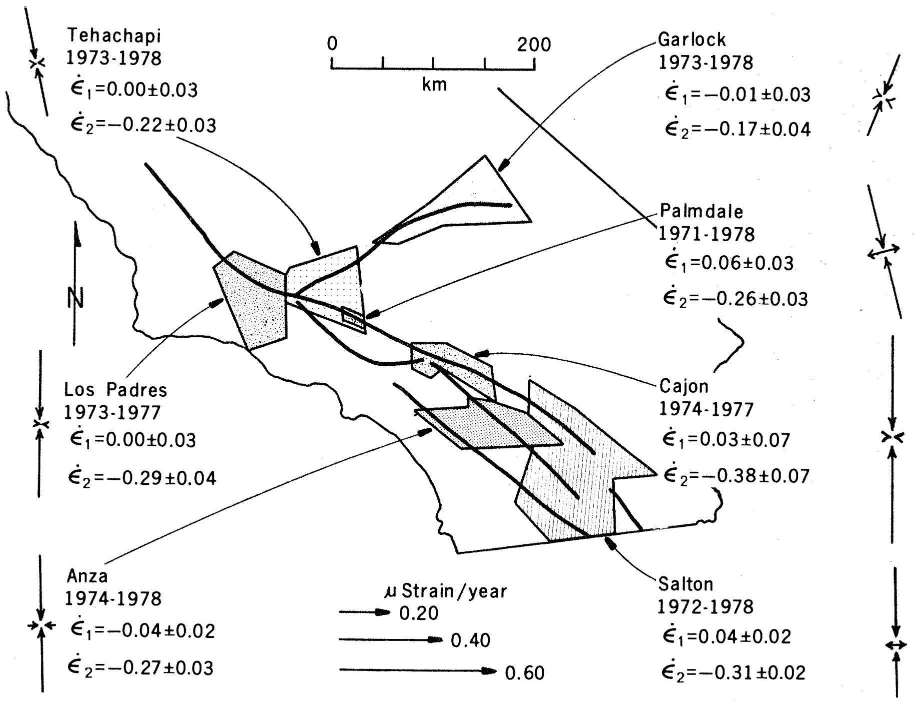

Fig. 1. Map of southern California showing the locations of the seven trilateration networks and the principal strains (in μstrain/year) measured at each. The heavy sinuous lines represent the major faults.

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