

CONVERTING AMS DATA TO RADIOCARBON VALUES: CONSIDERATIONS AND CONVENTIONS

A P McNichol

NOSAMS, Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543 USA. Email: amcnichol@whoi.edu.

A J T Jull • G S Burr

NSF Arizona AMS Facility, Physics Building, University of Arizona, Tucson, Arizona 85721 USA

ABSTRACT. We summarize the basic operation of accelerator mass spectrometry (AMS) systems used to measure radiocarbon and discuss the calculations used to convert AMS output to ^{14}C data.

INTRODUCTION

Natural-level radiocarbon measurements have proven invaluable to numerous fields of study including oceanography, geology, and archaeology. In the last 10 years, it has become apparent that the great majority of ^{14}C measurements are performed by accelerator mass spectrometry (AMS) in contrast to earlier decay-counting methods. It seems appropriate therefore to summarize the basic methods of the measurement and the calculations required to produce a useful ^{14}C measurement. More technical reviews of AMS exist (e.g. Linick et al. 1989; Fifield 1996; Donahue et al. 1990; Brown and Southon 1997) but there are no general discussions directed to the non- ^{14}C expert of how these results are obtained. In the course of our work, we are often asked by users for a summary of the methods employed. We hope this paper can serve that purpose.

The final result of an AMS measurement is an isotope ratio that is converted to a fraction of modern carbon. For the non-specialist, we describe the basics of an AMS measurement, how the operation of the accelerator affects a measurement, and how the accelerator output is used to calculate a fraction modern. The interested reader is also directed to the general treatment of AMS by Tuniz et al. (1998) and the more detailed calculations presented in the references cited here, particularly Donahue et al. (1990) for Arizona's operations and Schneider et al. (1994) for NOSAMS.

AMS Measurements

In AMS, one counts ^{14}C atoms while decay-counting methods count β particles. The two methods are often considered to be totally equivalent because the number of ^{14}C atoms can be related to activity through the radioactive decay equation. In both methods, the ultimate precision that can be obtained is limited by the number of events detected according to Poisson statistics ($s = n^{0.5}/n$), but precise results may be obtained more rapidly on 1/1000 to 1/10,000 as much material by AMS. However, there are operational differences, as we will discuss. AMS is fundamentally different from radiometric methods and requires different approaches and calculations to convert the output to a ^{14}C date. The main function of an AMS is to accelerate the different isotopes of carbon to a great enough velocity that mass 14 can be separated and distinguished from mass 12 and/or mass 13 and other rare particles with masses very close to ^{14}C , e.g. ^{13}CH and $^{14}\text{CH}_2$. For ^{14}C measurements, high energies allow the use of the accelerator to destroy any molecular ions and also to use nuclear detection methods (see Tuniz et al. 1998).

Measurement of ^{14}C in a Sample

An AMS is a sophisticated instrument that marries the techniques of particle physics with mass spectrometry. Figure 1 shows a schematic of the accelerator in operation at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility. We will use this figure to illustrate the basic operation of an AMS.

Any AMS ^{14}C measurement starts with the chemical conversion of carbon in a sample to CO_2 . Most laboratories then convert the sample CO_2 to filamentous carbon using a catalytic process (Baker and Harris 1978; Rutherford and Liner 1970; Guinot et al. 1981). This material is commonly referred to by AMS labs as “graphite”. The catalyst can be many metals, oxides, or other surfaces, but the best catalysts are Fe, Co, and Ni, and these are the catalysts generally used. The carbon is pressed into a target holder and placed in a sample carousel. The carousel, containing a suite of samples and standards, is placed in the accelerator’s ion source and evacuated. Usually around 15–20% of the carousel is filled with primary standards. A few laboratories directly introduce CO_2 into the accelerator’s ion source (Middleton et al. 1989; Bronk Ramsey and Hedges 1997) or are developing such capabilities (Schneider et al. 2000). To date, the best results are obtained with a solid carbon target.

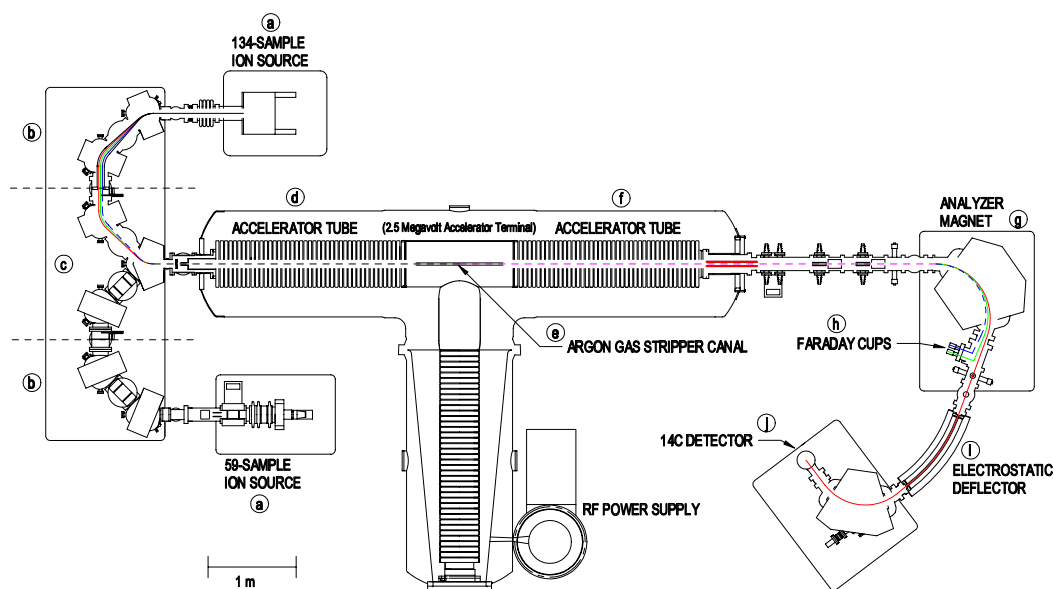


Figure 1 NOSAMS accelerator. See text for description of the figure.

There are many different mechanical configurations of ion sources available, but the basic function is the same. Carbon is converted to a single negatively charged ion by bombardment with a Cs ion beam in the ion source (see a in Figure 1). Atoms and ions are displaced from the sample by collisions, a process known as “sputtering”. An important reason AMS works well for measuring ^{14}C is that N, which is mostly mass 14 and is present in any vacuum system, does not produce a negative ion. In addition to producing C^- ions, other negative ions of the same mass as ^{14}C (e.g. $^{13}\text{CH}^-$, $^{12}\text{CH}_2^-$) are produced and must be removed at different stages in the accelerator. Prior to acceleration, the ion beams corresponding to masses 12, 13, and 14 are separated and higher and lower mass impurities are filtered out (b in Figure 1). Depending on the AMS design, some laboratories sequen-

tially inject, or pulse, either two or all three mass beams into the accelerator tubes. Laboratories injecting two beams usually inject masses 13 and 14. Other laboratories recombine two or three of the beams and inject them into the accelerator tubes (c in Figure 1). Simultaneous injection of the isotopes may reduce the error introduced when the pulsed beams experience accelerating potentials that are not identical due to the inherent operation of a system like this. In cases where all three masses are injected simultaneously, the mass 12 is usually reduced, or chopped, to approximately 1% of its initial size to avoid overloading the accelerator.

In the first stage of acceleration (d in Figure 1), the negative ion beams are accelerated to a high kinetic energy, 2.5 MeV kinetic energy at NOSAMS. After this acceleration, the beam encounters a stripping canal where electrons are stripped from the carbon ions. At NOSAMS and Arizona, a gas stripping canal is used and the +3 charge state is produced. The stripper also destroys some of the molecules that may mask as ^{14}C . The positively charged ions are then further accelerated (f in Figure 1) to an even higher kinetic energy, 10 MeV at NOSAMS. The beam is focused, passes through an analyzer magnet (g in Figure 1), and ^{12}C and/or ^{13}C currents are measured in Faraday cups (h in Figure 1). Recent studies using smaller accelerators have indicated that the ^{14}C separation can be done at energies as low as $\sim 1\text{MeV}$ and in the 1+ charge state (Suter et al. 2000).

After exiting the accelerator, further mass and energy separations are needed. An electrostatic deflector (i in Figure 1) transmits only particles with the proper energy and charge and another magnet removes more stray particles. Whether the electrostatic deflector is placed before or after the main analyzer magnet (g) depends on the individual accelerator. The final isotope selection process occurs in either a solid surface-barrier detector or a gas ionization detector (j in Figure 1). The detector discriminates particles based on each particle's total energy and rate of energy loss in the detector. Even with all these mass and isotope selection devices, there are still stray particles that may mask as ^{14}C , e.g. hydrides and dispersed ^{13}C and ^{12}C beams, and which may hit the detector. However, these ions will have a different energy from $^{14}\text{C}^{3+}$ and can be resolved in the detector.

The final result, or raw data, for each sample or standard consists of

- ^{14}C number of counts
- $^{12,13}\text{C}$ integrated charge collected.

The charge collected is converted to pulses using Coulomb's law and the charge of an electron and, then, a ratio of $^{14}\text{C}/^{12}\text{C}$ or $^{14}\text{C}/^{13}\text{C}$ is calculated. This ratio is used to calculate a fraction modern, the unit of ^{14}C measurement we will use in this paper.

Conversion of Raw Data to Fraction Modern

The "fraction of modern carbon" is determined by comparing the isotopic ratio of the sample to the standards, corrected to "modern carbon". "Modern" carbon is defined as the activity of ^{14}C in 1950 AD. Due to perturbation of the signal in 1950 AD by fossil-fuel carbon, the actual value was derived from 1850 AD wood, age corrected to 1950 AD (Stuiver and Polach 1977). The usual standards are oxalic acids I and II (HOxI, HOxII) from the US National Institute of Standards and Technology, which have a well-defined ratio to this value.

By definition, fraction modern equals

$$F_m = R_{\text{norm}}/R_{\text{modern}}, \quad (1)$$

where

R is the $^{14}\text{C}/^{12}\text{C}$ or $^{14}\text{C}/^{13}\text{C}$ ratio,

R_{norm} is the ratio normalized to $\delta^{13}\text{C}$ of -25‰ ,

$R_{\text{modern}} = 0.95R_{\text{HOxI},-19} = .7459R_{\text{HOxII},-25}$, and

$R_{\text{HOxI},-19}$, $R_{\text{HOxII},-25}$ refer to the internationally accepted values of R for HOxI and HOxII, as discussed by Donahue et al (1990).

Conversion of F_m to other commonly used ^{14}C units, such as pMC and ^{14}C age, is discussed in Stuiver and Polach (1977) (where R is analogous to an activity ratio, A) and Mook and van der Plicht (1999). Raw data are collected for standards surrounding a sample, the sample, a machine background sample and, usually, a sample used to identify the process blank. These data are converted to fraction modern in the following steps described below.

Step 1. Any machine background (MB) should be subtracted from the ratios measured (R_{meas}) on standards, samples, and process blanks.

$$R' = R_{\text{meas}} - R_{\text{MB}} \quad (2)$$

The machine background is the isotope ratio measured on a known ^{14}C -dead carbon material that has undergone *no* chemical processing. It provides a measure of the amount of extraneous matter that is detected as ^{14}C , e.g. scattered ^{12}C or ^{13}C beams, and/or carbon hydrides with the appropriate charge ($^{12,13}\text{CH}^{n+}$). Two important factors that can affect the machine background are the quality of the vacuum and the cleanliness of the ion source. This background is usually insignificant for AMS machines of $>2\text{MV}$ terminal voltage. However, for the new smaller $<1\text{MV}$ AMS machines (e.g. Synal et al. 1999) this may be a significant issue.

Step 2. Calculate the appropriate R_{modern} to use for the samples.

The isotopic ratio $^{14}\text{C}/^{13}\text{C}$ or $^{14}\text{C}/^{12}\text{C}$ for the sample is measured and compared to appropriate standards and corrected for stable carbon fractionation.

For labs measuring $^{14}\text{C}/^{12}\text{C}$

$$R_{\text{HOxI},-19} = R'_{\text{HOxI}} [(1 + -19/1000)/(1 + \delta^{13}\text{C}_{\text{HOxI}}/1000)]^2 \quad (3)$$

$$R_{\text{HOxII},-25} = R'_{\text{HOxII}} [(1 + -25/1000)/(1 + \delta^{13}\text{C}_{\text{HOxII}}/1000)]^2 \quad (4)$$

For labs measuring $^{14}\text{C}/^{13}\text{C}$

$$R_{\text{HOxI},-19} = R'_{\text{HOxI}} [(1 + -19/1000)/(1 + \delta^{13}\text{C}_{\text{HOxI}}/1000)] \quad (5)$$

$$R_{\text{HOxII},-25} = R'_{\text{HOxII}} [(1 + -25/1000)/(1 + \delta^{13}\text{C}_{\text{HOxII}}/1000)] \quad (6)$$

Where $\delta^{13}\text{C}_{\text{HOxI}/\text{HOxII}}$ are the values measured on the gas from which the standards were prepared. This assumes that there is no significant fractionation in the preparation of graphite.

Then

$$R_{\text{modern}} = 0.95R_{\text{HOx1,-19}} = .7459R_{\text{HOx2,-25}} \quad (7)$$

At many labs, the ratios measured on the standards surrounding a sample are linearly interpolated to calculate an average value for a standard that would have been measured at the time of the sample, e.g. Schneider et al. (1994). As sample carousels have become larger, it has become possible to design more sophisticated interpolation routines that use data from all the standards, and, sometimes, the samples (Seguin et al. 1994). Alternatively, the weighted mean of all the standards run in the same wheel is used as the mean standard for comparison.

Step 3. Calculate the uncorrected (uc) Fm for the measured sample (ms).

$$Fm_{\text{uc}} = R'_{\text{ms}}/R_{\text{modern}} \quad (8)$$

Step 4. Correct Fm for isotopic fractionation to obtain the measured fraction modern on the sample.

For labs measuring $^{14}\text{C}/^{12}\text{C}$

$$Fm_{\text{ms}} = Fm_{\text{uc}}[(1 + -25/1000)/(1 + \delta^{13}\text{C}_s/1000)]^2 \quad (9)$$

For labs measuring $^{14}\text{C}/^{13}\text{C}$

$$Fm_{\text{ms}} = Fm_{\text{uc}}[(1 + -25/1000)/(1 + \delta^{13}\text{C}_s/1000)] \quad (10)$$

Where $\delta^{13}\text{C}_s$ is the value measured on the gas from which the sample was prepared.

Step 5. Subtract process blank (PB).

It is at this point that most laboratories subtract the process blank. The process blank is the amount of carbon that is introduced to a sample during chemical processing. This is often evaluated or checked by measuring the Fm of a ^{14}C -dead material that has undergone chemical processing identical to the sample of interest. Operations of the accelerator should have no effect on the process blank unless its effect on the sample is smaller than the machine blank. In this case, the process blank will be indistinguishable from the machine blank. Removal of the effect of the process blank provides the final result for the sample. For samples of a standard size (defined here as containing >300 $\mu\text{g C}$), there are at least several methods in use.

Method 1 (Woods Hole method). At NOSAMS, we have determined the size (C) and fraction modern of the process blank (Fm_{pb}) for a number of different processes (e.g. Pearson et al. 1998). We combine this information with our knowledge of the sample size and a mass balance to calculate the final fraction modern of the sample (Fm_s),

$$Fm_s = (Fm_{\text{ms}}C_m - Fm_{\text{pb}}C_{\text{pb}})/C_s \quad (11)$$

Using this method, measuring the Fm of a ^{14}C -dead material that has undergone chemical processing identical to the sample allows one to check whether the amount and Fm of carbon one assumes is added to the sample is correct. After the mass balance correction, the Fm_s of the ^{14}C -dead material should be indistinguishable from the machine background.

Method 2 (Arizona method). The method used at the University of Arizona for blank correction was defined by Donahue et al. (1990). In this approach, we take into account both the size of the blank

and the difference in F_m between the blank contamination defined as F_{pb} (which is assumed to be modern) and the sample material as measured ($F_{m_{ms}}$).

In this approach, using the same symbols as in Equation (11),

$$F_m = F_{m_{ms}}(1+f) - f F_{pb} \quad (12)$$

where F_m is the corrected fraction modern, $F_{m_{ms}}$ is the measured fraction modern, F_{pb} is the fraction modern of the blank contamination and f is defined as:

$$f = f(1)/M \quad (13)$$

where $f(1)$ is the blank contamination observed in a 1mg sample, 0.003 ± 0.001 mg, and M is the mass of the sample carbon in mg. The value of f appears to be an inverse function of mass below about 1mg C, above 1mg C it appears that a different function may be more appropriate. F_{pb} is usually assumed to be contemporary carbon (currently $F_m=1.09$).

From these 2 equations, one can derive

$$F_m = F_{m_{ms}} [1 - f(1)/(F_{m_{ms}} - 1)] \quad (14)$$

which is Equation (26) in Donahue et al. (1990). It can be shown that Method 2 is the same as Method 1 after Method 1 has been modified to reflect the analysis of ^{14}C and ^{13}C , not ^{14}C and ^{12}C .

Method 3 (Identical sized blank). This method has been used by a number AMS laboratories. In this case, one measures the F_m of a ^{14}C -dead material that has undergone chemical processing identical to the sample and is the same size as the sample of interest. For samples in which the standard and sample are prepared in the same manner, the F_m measured on the ^{14}C -dead material is subtracted from the F_m measured on the sample,

$$F_m = R_{\text{std}}/R_{\text{modern}} \times (R_{\text{ms}} - R_{\text{pb}})/(R_{\text{std}} - R_{\text{pb}}) \quad (15)$$

where R_{ms} is the measured isotopic ratio, R_{pb} is the measured or assumed ratio for a blank sample and R_{std} is the isotope ratio measured in the standard.

Sample Error Determination

Most AMS laboratories calculate two different errors, referred to here as internal and external error, for each sample. The internal error (interr) is based on the total number of counts measured for the sample (ms), standards (std) and the machine blank (mb) and is calculated assuming Poisson statistics (e.g. Schneider et al 1994):

$$(\text{Interr}/F_{\text{ms}})^2 = [(N_{\text{ms}} + N_{\text{mb}})/(N_{\text{ms}} - N_{\text{mb}})^2] + [(N_{\text{std}} + N_{\text{mb}})/(N_{\text{std}} - N_{\text{mb}})^2] \quad (16)$$

The external error (exterr) is calculated to account for the effect variations inherent to the operation of an instrument as sophisticated as an AMS may have on a ^{14}C measurement. This is derived from the standard deviation of a succession of ratios measured at separate time intervals.

$$\text{Exterr} = \text{standard deviation of } n \text{ measurements}/(n-1)^{0.5} \quad (17)$$

The larger of the two errors is reported as the sample error. Finally, laboratories using both HOxI and HOxII as primary standards use the observed ratio of the two standards as a measure of the overall reliability of an entire carousel of samples as well as the AMS performance over time (e.g. Donahue et al. 1990b; Schneider et al. 1995).

Very Small Samples

Many laboratories have reduced the size of the samples that can be analyzed by AMS. It is important to realize that each accelerator and ion source must be calibrated to run very small samples (defined here as containing <math><100 \mu\text{g C}</math>). Not only is the effect of process blanks maximized for very small samples, but the measured isotope ratio may change significantly as well (Pearson et al. 1998). Although the basic characteristics of the change are similar from lab to lab (Figure 2), the details differ and each lab must be familiar with them. The easiest way to deal with the large ratio changes seen at very small sample sizes is to run small standards with small samples. A series of measurements of standards of different masses must be used to calibrate this effect. Brown and Southon (1997) asserted that this effect, reported by many labs, was an artifact of the blank correction assumptions. In their argument, they showed that if the blank could be defined as $\sim 0.4\text{--}0.5$ modern, then one could explain both the depression of the observed R in a small sample and the blank. Brown and Southon (1997) showed some results on $\sim 42\%$ modern wood which appears to support this claim. We have not yet found evidence to support this interesting proposal. The problem is that one cannot simultaneously determine the size of the blank and the F_m of the blank on one sample. There is also no rea-

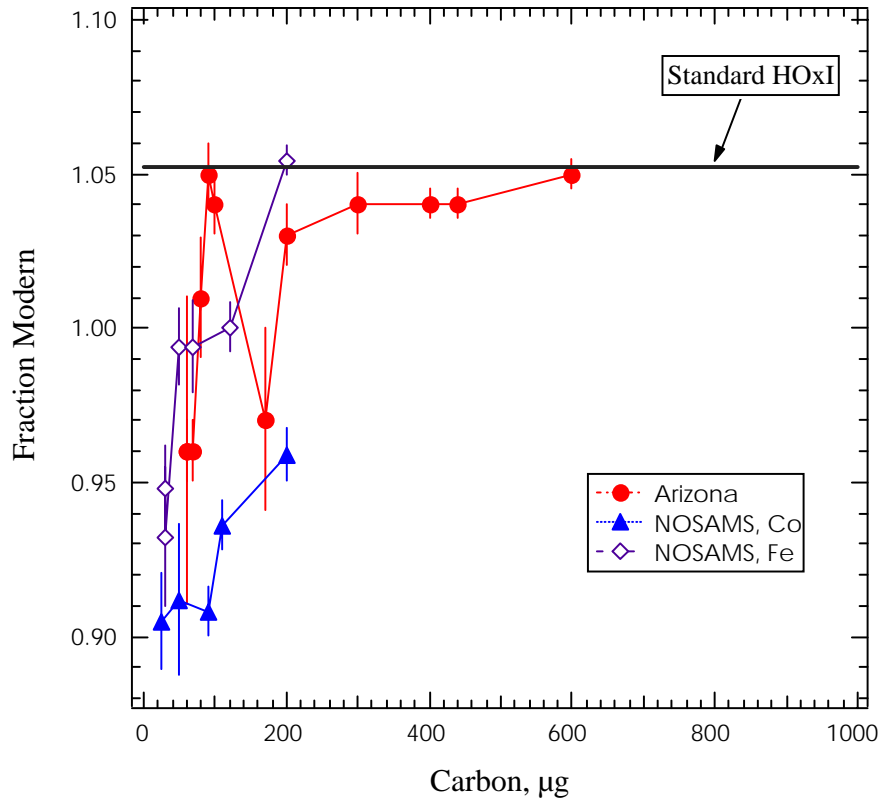


Figure 2 Fraction modern measured on small HOxI standards after normalizing to standard-sized HOxI. Results are shown for Arizona and for two different graphite catalysts used at NOSAMS. In practice, rather than try to derive an equation for the behavior of the standards, most laboratories run a large number of small standards with their small samples.

son a priori to state that Fm of the blank is independent of size. Further systematic studies along the lines proposed by Brown and Southon (1997) are need to determine the size and Fm dependence of blanks for very small samples. Unless these difficult measurements can be done for each particular situation, AMS measurements on small samples <100 µg will have errors due to the assumptions used concerning the blank corrections.

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