^{14}CHRONO

AMS Equations and Calculations

Contents

1. Starting with Stuiver and Polach….

We start with the Stuiver and Polach (1977) notation. A is the $^{14}C/^{12}C$ activity and subscripts S, OX refer to Sample and Oxalic respectively. Subscript N refers to a fractionation corrected quantity, but it will be dropped after the 2nd equation in favour of using [] which enclose the value to which the fractionation correction is made. Once the sample has been age corrected to 1950 the (1950) can also be dropped because the sample and the standard are measured at the same time.

$$F^{14}C = \frac{A_{SN}(1950)}{A_{ON}(1950)}$$

where

$$A_{SN}(1950) \equiv A_{S[-25]}(1950) \equiv A_S \cdot \frac{\left(1 - \frac{25}{1000}\right)^2}{\left(1 + \frac{\delta^{13}C_S}{1000}\right)^2}$$

$$A_{ON}(1950) \equiv A_{OX1[-19]}(1950) \equiv 0.95 \cdot A_{OX1} \cdot \frac{\left(1 - \frac{19}{1000}\right)^2}{\left(1 + \frac{\delta^{13}C_{OX1}}{1000}\right)^2}$$

First of all, we rewrite the equations using a normalization to OX2 instead of OX1. Stuiver (1983) relates the activity of OX1 and OX2 (his NOX) using

$$0.95 \cdot A_{OX1[-19]} = 0.7459 \cdot A_{OX2[-25]}$$

Therefore,

$$F^{14}C = \frac{A_{S[-25]}}{0.7459 \cdot A_{OX2[-25]}}$$

Because OX2 has $\delta^{13}C$ of -17.8 relative to PDB, we use another Stuiver (1983) result:

$$\frac{A_{X[a]}}{\left(1 + \frac{a}{1000}\right)^2} = \frac{A_{X[b]}}{\left(1 + \frac{b}{1000}\right)^2}$$

Giving

$$A_{OX2[-25]} = \left(\frac{1 - \frac{25}{1000}}{1 - \frac{17.8}{1000}}\right)^2 \cdot A_{OX2[-17.8]}$$

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Then

$$F^{14}C = \frac{A_{s[-25]}}{0.7459 \cdot \left(\frac{0.975}{0.9822}\right)^2 \cdot A_{OX2[-17.8]}} = \frac{1}{0.7459} \cdot \frac{1}{\left(\frac{0.975}{0.9822}\right)^2} \cdot \frac{A_s}{A_{OX2}} \cdot \left| \frac{\dfrac{.975}{1+\dfrac{\delta^{13}C_s}{1000}}}{\dfrac{.9822}{1+\dfrac{\delta^{13}C_{OX2}}{1000}}} \right|^2$$

Introducing the notation:

$$R0_x = A_x = \left(\frac{^{14}C}{^{12}C}\right)_x \quad \text{and} \quad R1_x = \left(\frac{^{13}C}{^{12}C}\right)_x = \left(1 + \frac{\delta^{13}C_x}{1000}\right)$$

where zero and one refer to the rare and abundant isotope in the notation favoured by NEC, we finally have

$$F^{14}C = \frac{1}{0.7459} \cdot \frac{R0_s/R1_s^2}{R0_{OX2}/R1_{OX2}^2}$$

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2. Nomenclature

The word **cathode** refers to the value obtained for the measurement of a carbon AMS target. We use the abstraction of a **run** to refer to a single exposure of the target to cesium. Typically there are 8 two minute exposures of the target to cesium, so the value for a **cathode** is obtained by averaging 8 runs. We also use the abstraction of a **sample** to refer to the average value of several cathodes of the same material. This is most often used for standards and backgrounds.

We use **avg** and **sig** for average and uncertainty (sigma). **R0** and **R1** refer to $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios respectively. When a **B** or **S** is inserted before the R it refers to that ratio for the Background or Standard.

In this notation the formula for the background and fractionation corrected quantity F14C for a run is

$$\text{avgF14C}_{run} = \frac{1}{.7459} \cdot \frac{\dfrac{\text{avgR0}_{run} - \text{avgBR0}}{\text{avgR1}^2_{run}}}{\dfrac{\text{avgSR0}_{run} - \text{avgBR0}}{\text{avgSR1}^2_{run}}}$$

3. F14C_{run} Calculation

We calculate the F14C value of a single run of an unknown with the following quantities: avgSR0 and avgSR1 refer to the R0 and R1 values of the selected Standard runs which bracket, in time, the run of the unknown. Since we use online $^{13}C/^{12}C$ ratios there is no need to calculate a δ^{13C} value for normalization, and we use avgR1 directly. avgR1^2 refers to the average of R1 squared rather than the square of avgR1. avgBR0 is the average $^{14}C/^{12}C$ ratio for all designated background cathodes.

$$avgF14C_{run} = \frac{1}{.7459} \cdot \frac{\dfrac{avgR0_{run} - avgBR0}{avgR1_{run}^2}}{\dfrac{avgSR0_{run} - avgBR0}{avgSR1_{run}^2}}$$

It is worth pointing out here that the fractionation correction is made to the background corrected value of the unknown's R0. The philosophy of the fractionation correction is that dividing by the $^{13}C/^{12}C$ ratio models a physical process. The background correction, on the other hand, is subtracting out the contribution to the sample of contamination due to chemistry in the laboratory and noise in the AMS. So we only fractionation correct that portion of the activity which occurred in nature.

Propagation of errors gives

$$\left|\frac{sigF14C_{run}}{avgF14C_{run}}\right|^2 = \left|\frac{sigR0_{run}}{avgR0_{run} - avgBR0}\right|^2 + \left|\frac{sigBR0}{avgR0_{run} - avgBR0}\right|^2 + \left|\frac{sigSR0_{run}}{avgSR0_{run} - avgBR0}\right|^2 + \left|\frac{sigBR0}{avgSR0_{run} - avgBR0}\right|^2$$

$$+ \ 2\cdot\left|\frac{sigR1_{run}}{avgR1_{run}}\right|^2 + 2\cdot\left|\frac{sigSR1_{run}}{avgSR1_{run}}\right|^2$$

having used

$$\left|\frac{sigR1^2}{avgR1^2}\right|^2 = 2\cdot\left|\frac{sigR1}{avgR1}\right|^2$$

The statistical uncertainty of each run is used to compute the uncertainty in the $^{14}C/^{12}C$ ratio:

$$sigR0_{run} = \frac{avgR0_{run}}{\sqrt{ncounts_{run}}}$$

There is no per-run uncertainty associated with R1 so $sigR1_{run}$ is taken as zero at this stage. Not until the runs have been averaged for a cathode is it possible to calculate a variance on the $^{13}C/^{12}C$ ratios. It is possible, however, to calculate a variance on SR1 for bracketing standards. The number of standards bracketing each run of a cathode is referred to as **nstandards**. The formulae for bracketing standards are:

$$avgSR0_{run} = \frac{\sum_{standards} R0_{standard}}{nstandards}$$

$$avgSR1_{run} = \frac{\sum_{standards} R1_{standard}}{nstandards}$$

$$sigSR0^2_{internal} = \frac{\sum_{standards} sigR0^2_{standard}}{nstandards^2}$$

$$sigSR0^2_{external} = \frac{\sum_{standards} \left(avgSR0_{standard} - avgSR0_{run}\right)^2}{nstandards \cdot (nstandards - 1)}$$

$$sigSR0_{run} = max\left(sigSR0_{internal}, sigSR0_{external}\right)$$

$$sigSR1^2_{run} = \frac{\sum_{standards} \left(avgSR1_{standard} - avgSR1_{run}\right)^2}{nstandards \cdot (nstandards - 1)}$$

4. F14C_cathode Calculation

Averaging the results of all the runs of a cathode to obtain a cathode average F14C is done with a weighted mean. The uncertainty is taken as the maximum of the internal error (counting statistics) and the external error (variance of all runs for a cathode).

$$\text{avgF14C}_{\text{cathode}} = \frac{\sum_{\text{runs}} \frac{\text{avgF14C}_{\text{run}}}{\text{sigF14C}_{\text{run}}^2}}{\sum_{\text{runs}} \frac{1}{\text{sigF14C}_{\text{run}}^2}}$$

$$\text{sigF14C}_{\text{internal}}^2 = \frac{1}{\sum_{\text{runs}} \frac{1}{\text{sigF14C}_{\text{run}}^2}}$$

$$\text{sigF14C}_{\text{external}}^2 = \frac{\sum_{\text{runs}} \left(\text{avgF14C}_{\text{cathode}} - \text{avgF14C}_{\text{run}} \right)^2}{\text{nruns} \cdot (\text{nruns} - 1)}$$

$$\left(\frac{\text{sigF14C}_{\text{cathode}}}{\text{avgF14C}_{\text{cathode}}} \right)^2 = \left(\frac{\max \left(\text{sigF14C}_{\text{internal}}, \text{sigF14C}_{\text{external}} \right)}{\text{avgF14C}_{\text{cathode}}} \right)^2 + 2 \cdot \left(\frac{\text{sigR1}_{\text{cathode}}}{\text{avgR1}_{\text{cathode}}} \right)^2$$

where

$$\text{avgR1}_{\text{cathode}} = \frac{\sum_{\text{runs}} \text{avgR1}_{\text{run}}}{\text{nruns}}$$

$$\text{sigR1}_{\text{cathode}}^2 = \frac{\sum_{\text{runs}} \left(\text{avgR1}_{\text{cathode}} - \text{avgR1}_{\text{run}} \right)^2}{\text{nruns} \cdot (\text{nruns} - 1)}$$

5. Comment on Background Correction

If R0 (14/12 ratio) of an unknown sample is less than the R0 of the designated backgrounds (ie F14C is negative) then the age is reported as a 'greater than' age. The value of the 'greater than' F14C is twice the uncertainty on the background. Stuiver and Polach are ambiguous on whether the sample uncertainty or the background uncertainty should be used here. See the discussion below.

If F14C of an unknown sample is within two sample F14C standard deviations of the designated background then the sample F14C is increased by twice its F14C uncertainty. The following formulas illustrate this:

$$
\begin{aligned}
&\text{if}\left(\text{avgF14C}<0\right) \\
&\quad \text{avgF14C}=2\cdot\text{sigF14C} \\
&\text{else if}\left(\text{avgF14C}<2\cdot\text{sigF14C}\right) \\
&\quad \text{avgF14C}=\text{avgF14C}+2\cdot\text{sigF14C}
\end{aligned}
$$

We estimate the uncertainty of our background measurement by determining the long term variance of our measured backgrounds and obtain a ratio of this variance with the long term average of our measured backgrounds. This ratio is multiplied with each day's measured background value and the result added in quadrature with the day's measured background uncertainty

The purpose of the next discussion is to look at the implications of an alternative way of making the background correction. This is to normalize the unknown to the standard before background correction. Starting with our original equation, one can make the following approximations:

$$
\begin{aligned}
\text{avgF14C} \;=\;& \frac{\dfrac{\text{avgR0}-\text{avgBR0}}{\text{avgR1}^2}}{\dfrac{\text{avgSR0}-\text{avgBR0}}{\text{avgSR1}^2}} \\[2em]
=\;& \frac{\dfrac{\text{avgR0}-\text{avgBR0}}{\text{avgR1}^2}}{\dfrac{\text{avgSR0}}{\text{avgSR1}^2}}\cdot\left|1-\frac{\dfrac{\text{avgBR0}}{\text{avgSR1}^2}}{\dfrac{\text{avgSR0}}{\text{avgSR1}^2}}\right|^{-1} \\[2em]
\simeq\;& \frac{\dfrac{\text{avgR0}-\text{avgBR0}}{\text{avgR1}^2}}{\dfrac{\text{avgSR0}}{\text{avgSR1}^2}}\cdot\left(1+\frac{\text{avgBR0}}{\text{avgSR0}}\right) \\[2em]
\simeq\;& \frac{\dfrac{\text{avgR0}}{\text{avgR1}^2}}{\dfrac{\text{avgSR0}}{\text{avgSR1}^2}}-\frac{\dfrac{\text{avgBR0}}{\text{avgR1}^2}}{\dfrac{\text{avgSR0}}{\text{avgSR1}^2}}+\frac{\dfrac{\text{avgR0}}{\text{avgR1}^2}}{\dfrac{\text{avgSR0}}{\text{avgSR1}^2}}\cdot\frac{\text{avgBR0}}{\text{avgSR0}}
\end{aligned}
$$

There are 3 orders of magnitude difference between the activity of the BKG and the STD so **unless the unknowns are fairly close to modern** one can neglect the term

$$\frac{\dfrac{avgR0}{avgR1^2}}{\dfrac{avgSR0}{avgSR1^2}} \cdot \frac{avgBR0}{avgSR0}$$

Therefore the approximate result is

$$avgF14C_{UNK} \simeq avgF14C'_{UNK} - avgF14C_{BKG}$$

where avgF14C[1] denotes an avgF14C that has not been background corrected. In other words, as an approximation, background subtraction can be done after normalization. This result means that the error propagation for the F14C uncertainty is as follows:

$$sigF14C^2_{UNK} = \left(\frac{sigF14C'_{UNK}}{avgF14C'_{UNK}}\right)^2 + \left(\frac{sigF14C_{BKG}}{avgF14C_{BKG}}\right)^2$$

This approximation has a significant impact on how the sigF14Cs are calculated. As shown above the error propagation of a difference is the sum of the squares of the terms. However, when the background is subtracted prior to normalization the final error propagation involves the quotient of terms and is proportional to the ratio itself. This means that if the activity of a sample is negative (due to being indistinguishable from background), the uncertainty is also negative. Stuiver and Pollach are not explicit about whether the uncertainty of the sample or the background is to be reported in that case, but certainly it appears that the background uncertainty is intended, since the sample uncertainty is negative, and therefore meaningless.

6. Comment on δ^{13}C Correction

Fractionation corrections in the $F^{14}C$ calculation are carried out with $^{13}C/^{12}C$ ratios measured concurrently with $^{14}C/^{12}C$ ratios. A $\delta^{13}C$ calculation is carried out for internal use, but is not made available with reported radiocarbon dates.

7. Calculation and Determination of Error Multipliers

For **k** replicate measurements $\mathbf{X_j}$ with uncertainty $\mathbf{S_j}$ of a single sample material, the square of the error multiplier is defined as

$$\Theta^2 = \frac{\Sigma_{j=1}^k \left(\frac{X_j - \mu}{S_j}\right)^2}{k}$$

where the error weighted mean μ is defined as

$$\mu = \frac{\Sigma_{j=1}^k \frac{X_j}{S_j^2}}{\Sigma_{j=1}^k \frac{1}{S_j^2}}$$

We determine an error multiplier for secondary standards of each sample type for which we have sufficient material to run replicates. Otherwise we assume an error multiplier of 1.20.

Sample_Type	pretreatment	errmult
bone, antler or tooth root	Collagen	1.30
wood	AAA	1.20
shell or other carbonates	Acid Etch	1.00

Appendix A: Stuiver and Polach (1977) Equations

	SAMPLE	OXALIC ACID
NET ACTIVITY; NORMALIZED FOR COUNTING VOLUME, MASS CHANGE, DILUTION, IMPURITIES, ETC. ACTIVITY IN COUNTS PER MINUTE	A_S	A_{Ox}
NORMALIZATION FOR ISOTOPE FRACTIONATION. ALL δ^{13} VALUES WITH REGARD TO PDB	$A_{SN}=A_S\cdot\left(1-\dfrac{2(25+\delta^{13}C)}{1000}\right)$	$A_{ON}=.95\,A_{Ox}\cdot\left(1-\dfrac{2(19+\delta^{13}C)}{1000}\right)$
ABSOLUTE INTERNATIONAL STANDARD ACTIVITY (OXALIC ACID ACTIVITY) CORRECTED FOR DECAY SINCE 1950		$A_{ABS}=A_{ON}\cdot e^{\lambda(y-1950)}$
x=YEAR OF GROWTH y=YEAR OF MEASUREMENT	λ in table always $(8267\cdot\text{yr})^{-1}$	

	GEOCHRONOLOGICAL SAMPLES	GEOCHEMICAL SAMPLES WITHOUT AGE CORRECTION	GEOCHEMICAL SAMPLES WITH AGE CORRECTION
PER MIL DEPLETION OR ENRICHMENT WITH REGARD TO STANDARD	$d^{14}C=\left(\dfrac{A_S}{A_{ON}}-1\right)1000‰$	$\delta^{14}C=\left(\dfrac{A_S}{A_{ABS}}-1\right)1000‰$	$\delta^{14}C=\left(\dfrac{A_S\,e^{\lambda(y-x)}}{A_{ABS}}-1\right)1000‰$
Equivalent Equation			$\delta^{14}C=\left(\dfrac{A_S\,e^{\lambda(1950-x)}}{A_{ON}}-1\right)1000‰$
PER MIL DEPLETION OR ENRICHMENT RELATIVE TO STANDARD NORMALIZED FOR ISOTOPE FRACTIONATION	$D^{14}C=\left(\dfrac{A_{SN}}{A_{ON}}-1\right)1000‰$	$\Delta^{14}C=\left(\dfrac{A_{SN}}{A_{ABS}}-1\right)1000‰$	$\Delta=\left(\dfrac{A_{SN}\,e^{\lambda(y-x)}}{A_{ABS}}-1\right)1000‰$
Equivalent Equation			$\Delta=\left(\dfrac{A_{SN}\,e^{\lambda(1950-x)}}{A_{ON}}-1\right)1000‰$
APPROXIMATE RELATIONSHIP	$\Delta^{14}C=\delta^{14}C-2(\delta^{13}C+25)\left(1+\dfrac{\delta^{14}C}{1000}\right)$	$\Delta^{14}C=\delta^{14}C-2(\delta^{13}C+25)\left(1+\dfrac{\delta^{14}C}{1000}\right)$	$\Delta=\delta^{14}C-2(\delta^{13}C+25)\left(1+\dfrac{\delta^{14}C}{1000}\right)$
Conventional radiocarbon age BP, based on 5568 yr. half life $\lambda=(8033\cdot\text{yr})^{-1}$	$t=-8033\ln\dfrac{A_{SN}}{A_{ON}}$		
ALWAYS REPORT	$\delta^{13}C$ and conventional radiocarbon age	$\Delta^{14}C$, $\delta^{14}C$, and $\delta^{13}C$	Δ, $\delta^{14}C$, and $\delta^{13}C$
OPTIONAL	$d^{14}C$ and $D^{14}C$	$\text{p.M.}=\dfrac{A_{SN}}{A_{ABS}}100‰$ *	

When year of collection z differs from year of measurement y, either A_S or A_{SN} should be replaced by respectively $A_S e^{\lambda(y-z)}$, $A_{SN}e^{\lambda(y-z)}$ or A_S and A_{SN} kept unchanged but oxalic acid corrected for decay between year of collection and 1950 only. This procedure is applicable only when marked in the table by an asterisk.

References

Scott et al. 2007. Error and uncertainty in radiocarbon measurements. *Radiocarbon.* **49** (2) 427-440

Stuiver M. and Polach A. 1977. Discussion: Reporting of ^{14}C Data. *Radiocarbon*. **19** (3) 355-363