

WORKSHOP ON ¹⁴C DATA REPORTING

MINZE STUIVER

Departments of Geological Sciences and Zoology,
University of Washington, Seattle, Washington 98195

The purpose of the workshop was to clarify any possible confusion related to the reporting ¹⁴C data. Two areas of concern, the use of the new NBS oxalic acid standard (Cavallo and Mann, 1980), and the reporting of marine sample ages, were singled out for detailed discussions.

The ¹⁴C activity of the "old" NBS oxalic acid standard has traditionally been normalized on a $\delta^{13}\text{C}_{\text{PDB}}$ value of -19 per mil. This value is close, but not necessarily identical to the $\delta^{13}\text{C}_{\text{PDB}}$ value of CO_2 gas obtained from oxalic acid by a random user. Differences will be small, however, and if the user does not have a mass spectrometer available for the ¹³C measurements, he can, at least for routine work, dispense with the fine tuning (normalization to -19 per mil) and use his actual oxalic acid counting rates without ¹³C correction.

The $\delta^{13}\text{C}_{\text{PDB}}$ value of CO_2 gas derived from the newly introduced second NBS oxalic acid standard is closer to -17 per mil. Sentiment was therefore voiced at the meeting to normalize the new standard to -17 per mil. Others were of the opinion that -19 per mil for both standards was more appropriate.

Initially, a majority of the attendees in charge of ¹⁴C laboratories expressed an interest in normalizing on a $\delta^{13}\text{C}_{\text{PDB}}$ value of -17 for the new standard. However, during further discussion, normalizing on a $\delta^{13}\text{C}$ value of -25 per mil was favored because the ¹³C normalization of samples and the new oxalic acid standard would then be identical.

To correct for ¹³C fractionation the oxalic acid count rate is multiplied with the approximate factor $\left(1 - \frac{2(\delta^{13}\text{C}_{\text{ox}} + b)}{1000}\right)$. For the old oxalic acid, b is 19 per mil. For the new oxalic acid, the discussions centered around a choice of 17, 19, and 25 per mil. The NBS report gives the ratio of the oxalic acid counts (Ox for the old, NOX for the new) when both are normalized to -19 per mil:

$$\text{NOX}(19)/\text{OX}(19) = 1.2894 \pm 0.0005.$$

The base-line (zero age activity) is obtained for the old oxalic acid by using the 0.95 OX(19) count rate. The corresponding expression for the new oxalic acid is $X(b)/\text{NOX}(b)$. For $b = 19$ per mil $X(19) = 0.7368$ when the preliminary NBS value is substituted. Thus, instead of taking 95 percent of the old oxalic acid value, equivalent results are obtained by taking 73.68 percent of the new oxalic acid count rate (when both are normalized on a ¹³C value of -19 per mil). The following relationships apply

Oxalic acid	$\delta^{13}\text{C}_{\text{PDB}}$	X(b)
Old	-19	0.95
New	-17	0.7338
New	-19	0.7368
New	-25	0.7457

The issue of normalization thus centers around the -17/0.7338; -19/0.7368, and -25/0.7457 combination. It is obvious that each laboratory can have its preferred $\delta^{13}\text{C}$ value as long as the appropriate b, X(b) combination is used.

An ambiguity in the use of radiocarbon ages was discussed also. Following Stuiver and Polach (1977) the term, conventional radiocarbon age, would imply ^{13}C normalization of all samples to the base of $\delta^{13}\text{C}_{\text{PDB}} = -25$ per mil. Thus, a conventional radiocarbon age would take into account ^{13}C fractionation but not differences in ^{14}C specific activity of reservoirs that arise from effects other than fractionation. A conventional radiocarbon age would be reported without adjustment and a reservoir corrected age would have to be given separately.

The major difficulty encountered with the above procedure is past reporting practices for archaeologic and geologic marine samples. The conventional radiocarbon age for marine materials only takes ^{13}C fractionation into account. Because the corrections for ^{13}C fractionation and reservoir ^{14}C deficiency cancel each other more or less for shells of mid- and low-latitude regions, many laboratories have adopted the convenient practice of deleting correction factors for both isotope fractionation and ^{14}C reservoir deficiency from their calculations. In that instance the radiocarbon age reported is a reservoir corrected age.

A majority of the participants felt that for all samples, including marine specimens, a conventional radiocarbon age based on the normalization to a $\delta^{13}\text{C}$ value of -25 per mil should be reported. Thus, a conventional radiocarbon age, as well as a reservoir corrected age, would be given. Although adopted, this proposal sparked strong opposition from the minority (ca 40 percent of the voting participants).

The various possible ways of correcting for isotope fractionation were also questioned. The fractionation factor for the distribution of ^{14}C between two compounds should be the square of the fractionation for ^{13}C (Craig, 1957) when possible effects of a molecular asymmetry are neglected. The use of this rule (Stuiver and Robinson, 1974) leads to an isotope fractionation corrected $\Delta^{14}\text{C}$ (normalized to a $\delta^{13}\text{C}$ value of -25 per mil) that is given by

$$\Delta^{14}\text{C} = 1000 \left[\left(1 + \frac{\delta^{14}\text{C}}{1000} \right) \frac{0.975^2}{\left(1 + \frac{\delta^{13}\text{C}}{1000} \right)^2} - 1 \right] \quad (1)$$

where $\delta^{14}\text{C}$ is the relative difference between the 0.95 oxalic acid standard and sample activity and $\delta^{13}\text{C}$ is the relative difference between the sample and PDB $^{13}\text{C}/^{12}\text{C}$ ratio.

A first order approximation of the above equation results in the commonly used equation:

$$\Delta^{14}\text{C} = \delta^{14}\text{C} - (2 \delta^{13}\text{C} + 50) \left(1 + \frac{\delta^{14}\text{C}}{1000} \right) \quad (2)$$

Another approximation uses the relative $\delta^{13}\text{C}$ deviation $(\delta^{13}\text{C} + 25)/\left(1 + \frac{\delta^{13}\text{C}}{1000}\right)$ (Mook, 1980)

$$\Delta^{14}\text{C} = \delta^{14}\text{C} - 2 (\delta^{13}\text{C} + 25) \left(1 + \frac{\delta^{14}\text{C}}{1000} \right) / \left(1 + \frac{\delta^{13}\text{C}}{1000} \right) \quad (3)$$

The $\Delta^{14}\text{C}$ values derived from equations 2 and 3 differ slightly from those obtained from equation 1. Equation 2 derived $\Delta^{14}\text{C}$ values differ less than 1 per mil from $\Delta^{14}\text{C}$'s derived from equation 1 when $\delta^{13}\text{C}$ ratios are in the -31 to $+3$ per mil range. For equation 3 the corresponding interval is -55 to $+6$ per mil. Outside this range the discrepancies increase more rapidly for equation 2 derived values than for those derived from equation 3.

For measuring precisions up to a few per mil, and $\delta^{13}\text{C}$ values in the 0 to -30 per mil range, any of the above equations can be used with good results. However, for high precision work (1 per mil or better), or when a wide range of $\delta^{13}\text{C}$ values is encountered, equation 1 is to be preferred.

In further action, the meeting adopted the AD 1950 absolute NBS oxalic acid disintegration rate of 14.27 ± 0.07 disintegrations per minute per gram of carbon. This corresponds with an activity for 95 percent of oxalic acid of 13.56 ± 0.07 disintegrations per minute per gram carbon, which gives a $^{14}\text{C}/\text{C}$ ratio of $(1.176 \pm 0.010) 10^{-12}$ (Karlén and others, 1968, first reported in 1964). The above activities are normalized on an oxalic acid $\delta^{13}\text{C}_{\text{PDB}}$ value of -19 per mil.

The $^{14}\text{C}/\text{C}$ ratio is important for the conversion to total ^{14}C ($\Sigma^{14}\text{C}$) of, for instance, ocean water:

$$\Sigma^{14}\text{C} = 1.176 \cdot 10^{-12} \left(1 + \frac{\Delta^{14}\text{C}}{1000} \right) \Sigma \text{CO}_2$$

where both $\Sigma^{14}\text{C}$ and ΣCO_2 are in μ mole/kg of sea water.

REFERENCES

- Cavallo, L M and Mann, W B, 1980, New National Bureau of Standards contemporary carbon-14 standards, in Stuiver, Minze and Kra, Renee, eds, Internatl radiocarbon conf, 10th, Proc: Radiocarbon, v 22, no. 3, p 962-963.
- Craig, Harmon, 1957, Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide: *Geochim et Cosmochim Acta*, v 12, p 133-149.
- Karlén, I, Olsson, I U, Källberg, P, and Kilici, S, 1968, Absolute determination of the activity of two ^{14}C dating standards: *Arkiv Geofysik*, v 4, no. 22, p 465-471.
- Mook, W G, 1980, The effect of fossil fuel and biogenic CO_2 on the ^{13}C and ^{14}C content of atmospheric carbon dioxide, in Stuiver, Minze and Kra, Renee, eds, Internatl radiocarbon conf, 10th, Proc: Radiocarbon, v 22, no. 2, p 392-397.
- Stuiver, Minze and Polach, H A, 1977, Discussion: Reporting of ^{14}C data: *Radiocarbon*, v 19, p 355-363.
- Stuiver, Minze and Robinson, S W, 1974, University of Washington Geosecs North Atlantic carbon-14 results: *Earth and Planetary Sci Letters*, v 23, p 87-90.