[RADIOCARBON, VOL 31, NO. 3, 1989, P 422–430]

^{14}CARE

HENRY POLACH

Radiocarbon Dating Research Unit, Research School of Pacific Studies
Australian National University, Canberra 2601, Australia

ABSTRACT. The need for and means of achieving a ^{14}C dating quality assurance service are debated.

INTRODUCTION

^{14}CARE is synonymous with *C*arbon dating *A*ccuracy *RE*port. Its purpose is the establishment of a quality assurance service that would assist laboratories engaged in ^{14}C dating consultations and research to reliably and quickly verify the quality of their work. Such verification is necessary since radiocarbon dating results may serve as a basis for worldwide correlations of events as well as economic, engineering and legal decisions. Equally important is the degree of confidence the user of the ^{14}C technique can assign a published ^{14}C date irrespective of whether it was determined for the laboratory as part of its own research activities or based on service (contractual or commercial) or collaborative research. The reliability of results and laboratory age determination reporting practices, therefore, need to be verifiably documented.

QUALITY ASSURANCE

The reliability of results is a function of precision and accuracy. Precision is related to reproducibility of results within a laboratory. It is determined internally, expressed as the standard error of determination. It is the only quality parameter the laboratory itself can give. To define accuracy (true ^{14}C value), however, always requires additional ^{14}C determinations and detailed attention to a number of factors such as alignment of the laboratory's relative ^{14}C determinations to an international standard, participation in interlaboratory comparisons, participation in interlaboratory quality verification programs, and unification of ^{14}C data reporting practices based on recommendations made by Stuiver and Polach (1977).

Radiocarbon Dating Standards

The internationally accepted primary reference standards for radiocarbon dating are the National Institute of Standards and Technology (formerly National Bureau of Standards), Washington DC, USA, Contemporary Standard for Carbon-14-Dating Laboratories, SRM 4990-B, and the *new* International Reference Material for Contemporary Carbon-14, RM 49/SRM 4900-C. These are referred to as NBS Oxalic (Ox) and NBS New Oxalic (NOx). Their calibration was the subject of international collaboration of selected ^{14}C dating laboratories (Godwin, 1959; Olsson, 1970; Cavallo & Mann, 1980; Mann, 1983).

An internationally accepted secondary standard is the Australian National University (ANU) Sucrose. Its relative value with respect to (wrt)

NBS Oxalic was also determined by selected ^{14}C dating laboratories (Polach, 1979; Currie & Polach, 1980).

A national secondary standard is the Chinese Charred Sucrose (Ch-Suc). Its calibration was undertaken by Chinese and selected western ^{14}C laboratories (Qui Xou hua *et al,* 1983). Table 1 lists the two primary and secondary reference standards and their values wrt AD 1950 (the ^{14}C reference year) and Table 2 shows their relative activity ratios.

TABLE 1

Internationally calibrated ^{14}C reference standards

Standard	δ^{13}C Measured range ‰ PDB	δ^{13}C Normalized ‰ PDB	"Modern" factor*	References
NBS-Ox	−14.0 to −22.0	−19.0	0.950	Godwin (1959); Olsson (1970)
NBS-NOx	−16.8 to −18.5	−25.0	0.7459	Stuiver (1983)
ANU-Suc	−10.0 to −13.0	−25.0	0.6631±0.002	Currie & Polach (1980)
Ch-Suc**	−18.0 to −25.0	nc	0.7342±0.003	Qui Xou hua *et al* (1983)

* The BP reference year (AD 1950) ^{14}C activity value is found by multiplying the δ^{13}C normalized reference standard net activity by the given "Modern" factor. *Note* that the primary reference standard values were defined by international agreement and therefore have no errors associated with their term. The secondary standards, however, based on cross-checks with the primary reference standard(s) must have an error term. The usage of ANU-Sucrose implies that this error is considered in the age calculations (Gupta & Polach, 1965, p 104).

** Chinese Charred Sucrose, not corrected (nc) for δ^{13}C value.

TABLE 2

Primary and secondary ^{14}C reference standard correction ratios

$NOx_{(-25)}/0.95Ox_{(-19)}$	1.3407±0.001	Mann (1983)
$ANU\text{-}Suc_{(-25)}/0.95Ox_{(-19)}$	1.5081±0.002	Currie & Polach (1980)
$Ch\text{-}Suc_{(nc)}/0.95Ox_{(-19)}$	1.3620±0.003	Qui Xou hua *et al* (1983)

The use of internationally accepted primary or secondary standards does not in itself guarantee accuracy. Cross-check and calibration studies (eg, Polach, 1972, 1979; Cavallo & Mann, 1980; Otlet *et al,* 1980; Scott, Baxter & Aitchison, 1981; Burleigh, Leese & Tite, 1986; Scott *et al*, 1988) have shown that a bias can and will occur. This bias is primarily due to malpractices such as: not periodically and frequently (several times each year) testing *freshly prepared, internationally accepted,* standard and background samples; using a local standard of doubtful value; not individually calibrating detectors or counting vials in radiometry; variable contamination during target preparation and fractionation during accelerator mass spectrometry (AMS) determinations. Other factors may affect the results even in the hands of experts: δ^{13}C ratio determination errors, δ^{14}C activity determination errors, variable carbon isotope fractionation of the oxalic acid standard (Grey *et al,* 1969; Polach & Krueger, 1972), variable fractionation during

purification or syntheses involved in radiometry, presence of impurities in the sample and the counting medium or instability and interference to counting equipment.

For these very reasons, leading ^{14}C laboratories have engaged in additional interlaboratory comparisons, hence quality assessment of their determinations (eg, de Jong, Mook & Becker, 1979; Baillie, Pilcher & Pearson, 1983; Pearson & Stuiver, 1986; Bonani *et al,* 1987). Such quality assessment measures were not always published (Tamers, pers commun, 1979) and when published, were not necessarily readily identified as accuracy control measures by the user or other ^{14}C laboratories as they were carried out in the context of validation of a specific, often very specialized, study or phase of research. Another example of quality assessment and validation is the testing of the ^{14}C method against other dating methods: U/Th, K/Ar and thermoluminescence (eg, Chappell *et al*, 1974; McDougall, Polach & Stipp, 1969; Stuiver, 1978; Prescott *et al,* 1983). The question that now must be asked is, "Was the question, 'Is radiocarbon dating obsolescent for archaeologists?' (Ottaway, 1986) answered?"

Interlaboratory Comparisons

Voluntary and anonymous participation in organized interlaboratory cross-checks are often the basis of comparative studies. These invariably determine that agreement as well as discrepancies between ^{14}C dating laboratories can and will arise. However, these anonymous cross-checks have:

- Not determined the causes of such discrepancies (although any student of ^{14}C dating can readily list possible causes even without reference to the cross-check results).
- Not guaranteed that participating laboratories have taken corrective measures. Their results as well as action to correct discrepant results remain predominantly anonymous.
- Not led to user or peer group confidence as, by nature of the anonymous and limited participation, the average user and average laboratory cannot determine who produces valid (always?), biased (systematically erroneous) or invalid (randomly erroneous) results at a given time.
- Not led to an unbiased assessment of validity and merit of the bulk of ^{14}C dating.
- Not led a user-recognized and laboratory-subscribed *^{14}C dating quality assurance* such as is practiced for chemical and isotope analysis by the International Atomic Energy Agency Analytical Quality Control Service Laboratory, Vienna.

Quality Assessment

Accuracy of ^{14}C dating determinations cannot, for practical reasons, be checked internally without access to a source of reference material additional to the already available, internationally accepted, primary and secondary ^{14}C dating and ^{13}C mass spectrometric standards. Such reference material is at

present not available. In order to serve the purpose of quality assurance, the new reference material needs several desirable characteristics. It should:

- Be a substance that can be used by all ^{14}C laboratories irrespective of age determination techniques (eg, AMS or radiometry) and be readily converted to CO_2.
- Have a ^{14}C activity that is 1) normally analyzed by all ^{14}C daters, 2) readily variable, 3) unknown to all except the producer, 4) determinable by a different method of analysis than AMS and low-level counting assays.
- Be readily available, of very high purity, have a precisely known and invariable carbon grammolecular weight concentration, be homogeneous, non-explosive, non-toxic, have a determinable $\delta^{13}C$ ratio on aliquots, be readily prepared in bulk, reproducible, cheap, transportable, storable, not deteriorate with age, remain uncontaminated during storage, sampling and transport, not be subject to isotopic fractionation on normal handling and routine preparation (eg, combustion) for ^{13}C and ^{14}C content determinations.
- Be prepared, distributed and results verified by an agent or agency of impeccable reputation in close collaboration with representatives from participating laboratories to protect the participants against errors.
- The organizing agency or person(s) must also be prepared to follow up with expert advice and counsel by drawing on available expertise.

When such a quality control reference material becomes available and leading ^{14}C dating laboratories agree to participate and, jointly and openly, make their data available for publication in an internationally known and relevant journal such as RADIOCARBON, then, it is my belief that, the demand from users and peer groups will result in more and more ^{14}C laboratories agreeing to verifiably document the quality of their work, thereby ensuring the global validity of their ^{14}C activity determinations.

Some Practical Considerations

A gas, liquid or concentrated solution of a quality-control reference sample can be found that will meet all specifications. It can be stored in bulk as 1) a ^{14}C-labeled (equivalent to contemporary environmental activities), and 2) an unlabeled (^{14}C background). Mixing the two, in proportions precisely determined by gas dilution or gravimetric techniques, would ensure that a variable ^{14}C-labeled set of samples, the *relative* $\delta^{14}C$ content of which is determined by other techniques than AMS or low-level radiometry, and the $\delta^{13}C$ content of which is reliably determined by mass spectrometry, is available for distribution.

Participating laboratories would receive a set of "unknown samples" to determine 1) their $\delta^{13}C$ values, 2) their δ and $\Delta^{14}C$ activity ratios and 3) the relative $\Delta^{14}C$ abundance wrt NBS Ox or NOx of the *Certified Reference Material* sample set submitted to them. (The nomenclature is as per Stuiver & Polach, 1977).

The agreement of the ^{14}C determination results received from a particular laboratory with the mean value obtained from statistical evaluations of

all results will be a measure of the accuracy of a particular determination wrt to the NBS standards.

Agreement of the ^{14}C activity ratios with those determined, by independent means, by the distributor or distributing agency will be a measure of internal laboratory precision.

Agreement of the $\delta^{13}C$ determinations will serve the additional purpose of validating ^{14}C results. Where laboratories have no need to determine $\delta^{13}C$ values, which is the case in certain circumstances only, then the interpretation of all results can be based on $\delta^{14}C$ determinations (*ie,* uncorrected for $\delta^{13}C$).

The distributor or agency would prepare the results for publication upon receiving written permission to do so from the participating laboratory. The regular (yearly) publication of agreement between participants would show that they ^{14}CARE. Literature reference to participation in ^{14}CARE programs would provide a *verifiable quality assessment as anonymous results would not be published.* Participants would be entitled to use the ^{14}CARE logo with the year of testing (eg, ^{14}CARE 1989) on their letter heads and age reports, thus contributing to user (customer) awareness of the quality assurance program. Such a protocol would ensure the integration within and confidence of other sciences; archaeology, eg (Waterbolk, 1983; Ottaway, 1986; Taylor, 1987; Wendorf, 1987) as well as contribute to the unity of science (Damon, 1970).

There will have to be a reasonable charge for the *Certified Reference Material* sample set, evaluation and publication of the results. There will be no limitation on the number of sample sets an individual laboratory can purchase or timing and frequency of participation. A certificate will be issued to all laboratories relating to the Certified Reference Material *immediately* after the submission of their final results. Results of ^{14}CARE Programs would be validated by a team of ^{14}C dating specialists preferably operating under the auspices of an international organization. The results would be published annually in RADIOCARBON. A task force can be recommended by the agency to assist those who wish to establish new laboratories or face difficulties.

My efforts will now be directed towards enlisting the cooperation of research scientists and/or seeking the support of an international institution to examine the ^{14}CARE idea. Once agreement has been reached and the practicality of the idea tested, then the protocol of the ^{14}CARE program can be defined and published. Only then could one enter into contractual testing on a broader scale.

ACKNOWLEDGMENTS

The draft of this manuscript was critically read and valuable advice and supportive comments were received from: P Airey, M Barbetti, P Becker-Heidemann, R Beukens, G Calf, J Chappell, L Currie, D Donahue, H Erlenkeuser, P Fritz, J Golson, R Gonfiantini, J Head, L Kaihola, R Kalin, H Kojola, B Kromer, A Long, M Manning, W Mook, K-O Münnich, B O'Brien, R Otlet, H Rast, W Rauert, S Robertson, K Rozanski, D Srdoc, J Stipp, M Tamers, B Thom, J Walker, H Willkomm, M Wolf and W Wölfli.

Valuable critical comments were received from M Geyh, D Harkness, G Pearson and H Scharpenseel. The references were verified by D Polach. The manuscript was prepared for publication whilst the author was a Visiting Professor (Feb–July, 1988) at the Institut für Hydrologie, GSF München.

Note added in press:

The International Atomic Energy Agency, Vienna, has agreed to coordinate the preparation of bulk ^{14}C dating reference material (ranging in age from modern to background), its calibration by dating laboratories, and its distribution as the *"Known ^{14}C Age Reference Samples"* (Rozanski, 1989).

A team of researchers (R Beukens, L Currie, B Kromer, A Long and R Kalin, R Otlet and J Walker, W Mook, and H Polach and S Robertson) have agreed to collaboratively investigate the suitability of isopropyl alcohol as the ^{14}CARE program's *Certified Reference Material.*

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II. CARBON CYCLE IN THE ENVIRONMENT

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