

IS COMPARABILITY OF ^{14}C DATES AN ISSUE?: A STATUS REPORT ON THE FOURTH INTERNATIONAL RADIOCARBON INTERCOMPARISON

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ABSTRACT. For more than 15 years, the radiocarbon community has participated in a series of laboratory intercomparisons in response to the issue of comparability of measurements as perceived within the wider user communities (Scott et al. 1990; Rozanski et al. 1992; Gulliksen and Scott 1995; Scott et al. 1997). In this report, we provide an update on the current ^{14}C laboratory intercomparison and reflect on future issues linked to the laboratory intercomparison program, not least those resulting from a significant growth in the number of accelerator mass spectrometry (AMS) facilities providing routine dating of small samples (milligram size).

INTRODUCTION

Comparability of radiocarbon age measurements has long been seen by laboratories and users as an important issue. As the availability of routine accelerator mass spectrometry dating has become more widespread, questions and doubts have been raised concerning the comparability and reliability of radiometric dating and accelerator mass spectrometry (AMS). Occasionally, and in some circumstances, significant differences have been observed between the radiometric and AMS measurements.

The ^{14}C community has been involved in an extensive program of intercomparisons with the most recent example (FIRI) having the objectives of:

- Demonstration of the comparability of routine analyses by both AMS and radiometric labs;
- Quantification of the extent of, and sources of, any variation;
- Investigation of the effects of sample size, pretreatment and precision requirements on the results.

The issues of comparability and reliability go beyond the basic metrological principle, and must confront the differing sample size requirements of AMS and radiometric methods. In the following sections, we describe the current laboratory intercomparison and explore how it tackles comparability.

The Current Intercomparison (FIRI)

As in previous intercomparisons (Gulliksen and Scott 1995), FIRI has focused on the use of natural materials, and has also implemented a two-stage design, with a set of core samples and a set of optional samples. In addition, two samples were identified for sample size and precision investigations.

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The core samples comprised a total of 10 samples of 5 materials; wood, barley, humic acid, cellulose and turbidite.

Wood samples

Approximately 10 kg and 12 kg of dendro-dated wood (comprising 20 and 40 rings, respectively) were cut to appropriate sizes (at least 40 g for radiometric and at least 4 g for AMS) before being labeled and bagged. Other wood samples were subdivided to appropriate sample sizes (approximately 50 g and 5 g, respectively for radiometric and AMS labs).

Two cellulose samples were also prepared from dendro-dated wood (16 kg and 10 kg, respectively) using an acid/alkali/acid procedure followed by bleaching using sodium chlorite. The extract was then washed, dried at 40 °C, physically mixed and then packaged into samples of 10 g and 1 g, respectively for radiometric and AMS laboratories.

Other Materials

Turbidite carbonate (mainly coccolith calcite) was taken from a single distal turbidite, derived from the middle ungraded deposit. The sample was immediately oven dried (approximately 50 °C), ground and fully homogenized before being bagged (sample size approximately 100 g and 10 g, respectively) and labeled.

A **humic acid** sample from a coastal cliff deposit at St Bees Head in Cumbria, northwest England which has been exposed by erosion was also prepared. A large peat sample was digested in 2% KOH at 80 °C. The alkali extracts were filtered and combined into a large container until over 150 L of solution were obtained. The bulk aqueous solution was then thoroughly mixed and the humic acid precipitated by adjusting the pH to 3 by the stirred addition of 2M H₂SO₄. The solid precipitate was then recovered by filtration and given a preliminary wash with cold distilled water. It was then re-dissolved, re-precipitated and dried. After drying to a constant weight, the crystalline humic acid was washed free of sulfate inclusions with hot distilled water. The sample was then re-dried and ground to obtain a relatively standard size of crystal. Samples for radiometric and AMS measurement are approximately 10 g and 1 g, respectively.

Barley mash is produced as a by-product of whisky manufacture. A sample (approximately 15 kg) from the current year was force dried and physically mixed. Samples are of approximately 50 g and 5 g, respectively, for radiometric and AMS laboratories.

Optional Samples

The optional samples included two wood samples (one dendro-dated), a whole peat sample (linked to the humic acid core sample) for both AMS and radiometric analysis and three separate mammoth tusks spanning the ¹⁴C age range, leather and fabric from a scythian burial and parchment for AMS analysis only.

Homogeneity Testing

The key sample requirement in an intercomparison is that of homogeneity, which simply means that any sub-sample, taken randomly from the bulk material is representative of that material and that when dealing with trace element assay, that the trace element is uniformly distributed throughout the bulk material.

Each material (with the exception of the dendro-dated wood) was independently tested in two laboratories (where possible a radiometric and an AMS laboratory). A minimum of eight analyses was required for homogeneity testing of each core material. Homogeneity testing for the barley mash was carried out by radiometric analysis at the SUERC ^{14}C laboratory, East Kilbride and ^{14}C laboratory, University College Dublin, for the first of the cellulose samples, homogeneity testing was carried out by radiometric analysis at the SUERC ^{14}C laboratory, East Kilbride, and at the ^{14}C laboratory of the Weizmann Institute.

For the turbidite, homogeneity testing was carried out by radiometric and AMS analysis at the National ^{14}C laboratory, NUST, Trondheim and Tandem accelerator laboratory, University of Uppsala. For the second cellulose sample, homogeneity testing was carried out by radiometric analysis at the KIK ^{14}C laboratory, Brussels and by AMS at the ^{14}C laboratory, University of Groningen. For the humic acid sample, homogeneity testing was carried out by radiometric and AMS analysis at the NERC ^{14}C laboratory, East Kilbride and AMS laboratory, University of Aarhus.

The results of the homogeneity testing were satisfactory and are being reported separately.

Current Status of FIRI

All core samples were distributed in September 1999, the deadline for results being August 2000. Currently over 80 sets of results have been returned and their analysis is underway. The full analysis was presented and discussed at an FIRI workshop in March 2001.

Optional samples are currently being distributed to participating laboratories.

Future Needs

There is still a need in routine dating for regular checks which can be satisfied by materials such as the IAEA reference materials and by programmes such as TIRI and FIRI which are directed more at large sample dating, but there is clearly also a need for further exploration of comparability and variation at the limits of the technique (very small or very old samples).

The issue of sample homogeneity becomes more and more important, indeed the definition of a sample becomes critical as smaller and smaller (compound specific) samples are dated. There are difficulties in taking a representative sub-sample from the bulk material. Indeed how do we know it is representative? Do we fully know the potential scale of natural ^{14}C variation in sample matrices?

Continuation in this work is important, the linkage to previous work provides an invaluable continuity (e.g. IAEA and other reference materials are still available and should be used), but in addition, further new materials should be sought, and these should include known age material. For the conventional laboratory, the typical sample requirement might be 5 g C with sample age ranges from <1 to approximately 7–8 half-lives. However, for the AMS labs and for those conventional labs where small samples are dated, we need to explore the natural variation in reportedly single event samples (deposits of charcoal, grain from a single growing season, single insects from a well defined stratum). This information is not just important for the laboratory, but is also of fundamental importance for the sample submitter who must select samples referring to the event of interest. Future inter-comparisons therefore will see some shift in emphasis to reflect these challenging issues.

CONCLUSIONS

In general, past intercomparisons have shown direct comparability of the AMS and radiometric laboratories but have also emphasized the potential variation that can be observed as a result of the sam-

ple heterogeneity, a feature which gains increasing prominence as the sample size requirement decreases. In the current laboratory intercomparison, comparability still remains the major issue, but the emphasis has shifted from comparability of the measurement to the more difficult issue of comparability of the samples and sampling. A full report on FIRI will be available by the end of 2001 and a special issue of this journal will appear in 2002.

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