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HIGH-PRECISION INTERCOMPARISON AT ISOTRACE

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ABSTRACT. I conducted a high-precision comparison at the 0.2% to 0.3% level with samples supplied by the radiocarbon laboratory of the Quaternary Research Center at the University of Washington (QRC). Four samples with ages ranging from modern to > 50,000 BP were dated in a blind test. The absence of cosmic-radiation background in AMS dating is a major advantage for dating samples > 35,000 BP. The reliability of AMS dates > 35,000 BP depends entirely on understanding the contamination processes. By comparing results with laboratories capable of sample enrichment, such as QRC, it is possible to identify and estimate the intrinsic ^{14}C in the background samples as well as the contamination introduced by sample preparation.

INTRODUCTION

Beukens, Gurfinkel and Lee (1986) tested precision and accuracy at the start of operations of the IsoTrace Laboratory. I demonstrated precision at the 0.25 – 0.37% level in reproducibility measurements, which showed that the precision, calculated from all known random errors, accounted for all the variance in the data. The intercomparison with samples from the Geological Survey of Canada (GSC) and the Australian National University (ANU) radiocarbon dating facilities showed good agreement at the 1% level, but several discrepancies did exist. Although some of these could be attributed to the way the GSC shell ages were reported (normalized to a base of $\delta^{13}C = 0‰$), discrepancies for some of the older samples were evident. Subsequently, I observed occasionally similar discrepancies on other samples. To understand the cause of these discrepancies and to test our laboratory at high precision, I initiated a four-part research program:

1. Determination of the machine background
2. Determination of the contamination contributed by sample preparation
3. Intercomparison of old and background samples with the GSC
4. High-precision intercomparison at the 0.2% level.

Analysis Procedures. All samples, analyzed as part of this program, contained 200 – 300μg of carbon. Prior to analysis, each sample was cleaned for 10 minutes with the primary cesium sputter beam. To avoid cratering during the analysis, I measured 16 spots on a sample. For every spot, the $^{14}C^{+3}$ ions were accumulated for 10 seconds while the $^{12}C^{+3}$ and $^{13}C^{+3}$ currents and their variances were determined before and after the measurement. This process was repeated for all samples, including the standards, 12 – 20 times until sufficient precision was obtained. I obtained conventional radiocarbon dates, corrected for natural and sputter fractionation to base of $\delta^{13}C = -25‰$, by comparison with the averaged results of 2 or 3 NBS I oxalic acid standards, as described previously (Beukens, Gurfinkel & Lee 1986). The measurements were conducted over a sufficiently long period to obtain finite results and avoid bias due to Poisson statistics. I reprocessed and remeasured every sample at least once and the results presented here are the weighted averages of these measurements. The background samples, in particular, were measured several times over a period of several months. No time-dependent variations were observed in these measurements, but remeasurements are being performed on a regular basis as a quality check. All results are presented without background or contamination corrections unless otherwise specified.

MACHINE BACKGROUND

Machine background in Accelerator Mass Spectrometry (AMS) is due to electronic noise, ion source contamination and ^{12}C ions from the $^{12}C^{-}$ sputter tail, mimicking ^{14}C ions (E/q ambiguity).

At the IsoTrace AMS facility, this last contribution is eliminated by a 45° electrostatic analyzer after the ion source. Electronic noise can be measured separately and was shown to contribute < 0.001 pMC to the background. Ion source contamination appears to be unavoidable because at least 90% of all sputtered ^{14}C is deposited somewhere in the source region. It can be minimized, however, by thorough cleaning and a proper ion source design. I measured the contribution of this contamination to the apparent age of an infinitely old sample on blank aluminum sample holders that yielded 0.002 ± 0.001 pMC or an apparent age of 85,000 ± 4000 BP.

CONTAMINATION DUE TO SAMPLE PREPARATION

I measured this contamination by preparing and analyzing samples that are geologically very old. Most old materials, however, are not free of intrinsic ^{14}C contamination because such samples can easily be contaminated during their long period of interment or during conservation after excavation or retrieval. As it is impossible to predict this contamination, many samples had to be analyzed to determine which were best suited for this purpose. Table 1 shows the current results of this contamination study.

Sample preparation at AMS facilities can be divided into two stages. The first stage consists of sample pretreatment and conversion into CO_2 either by acid hydrolysis of carbonates or combustion of organics. The second stage consists of the conversion of CO_2 into graphite. The pretreatment, combustion and hydrolysis techniques used here, are identical to those employed for any submitted sample and have not changed appreciably over the last five years. The lower ^{14}C levels in these measurements should therefore be attributed entirely to the lower intrinsic ^{14}C contamination of these samples and not to changes in sample preparation or analysis techniques.

TABLE 1
Sample-preparation-related background measurements

Sample treatment	Material	^{14}C content (pMC)	Apparent age (yr BP)
Graphitization	CO_2 from natural gas	0.077 ± 0.005	57,630 ± 540
Acid hydrolysis	Marble	0.076 ± 0.009	57,690 ± 920
Combustion	Wood fragment (Yukon)	0.152 ± 0.025	52,140 ± 1310
	Fossilized redwood (Axel Heiberg Island)	0.211 ± 0.018	49,490 ± 680

At IsoTrace, the graphitization process is different from that of other AMS laboratories. I first convert the CO_2 into acetylene using the standard Li-carbide synthesis. The acetylene is then dissociated in an electrical high voltage AC discharge and produces two machine-ready samples at one time (Beukens & Lee 1981). Industrial CO_2, produced by the combustion of natural gas, yields an apparent age of 57,630 ± 540 BP or 0.077 ± 0.055 pMC. Thus, this value represents the upper limit for the contamination contribution of the graphitization process.

Many carbonate samples were analyzed to test the combined contamination contribution of acid hydrolysis and graphitization. For several years, I obtained results of 0.15 to 0.13 pMC for optical grade calcite (Iceland Spar) and a carbonate aggregate from the upper Amazon region. Recently, a marble has yielded a result of 0.076 ± 0.009 pMC, equivalent to an apparent age of 57,690 ± 920 BP. This upper-limit estimate for the combined acid hydrolysis and graphitization processes is statistically identical to that of the graphitization process alone.

I obtained an upper limit of 52,140 ± 1310 BP or 0.15 ± 0.02 pMC for the combined contribution of the combustion and graphitization processes, on the cellulose fraction of a wood

sample submitted to the laboratory. As this was a surface find from an old shoreline of ancient Lake MacKenzie (Yukon, Canada) it is not exactly the most ideal sample and better suited material will surely be found. One sample that I expected to be the ideal blank is a well-preserved redwood sample from early Tertiary fossil forests on Axel Heiberg Island (North West Territories, Canada). The result (Table 1) was very disappointing, however, as the ^{14}C content of this sample is significantly higher than that of the first wood sample, implying that the Axel Heiberg wood sample is contaminated.

INTERCOMPARISON WITH THE GEOLOGICAL SURVEY OF CANADA

As part of the search for suitable background material, I re-analyzed calcite and anthracite background samples from the GSC, using identical pretreatment procedures. The GSC assumes these samples to be ^{14}C-free and subtracts their count rates from the samples, analyzed in their facility. This is intended to provide a correction for the cosmic radiation and electronic background as well as a correction for sample preparation-induced contamination. However, the IsoTrace re-analysis of these samples (Table 2) clearly shows that these samples are not ^{14}C-free because they yield higher ^{14}C contents than the limits in Table 1. This means that the GSC dates are over-corrected, resulting in ages that are too old. This fact is demonstrated by the re-analysis of the CO_2 from a shell and a wood sample for which the GSC quotes ages of > 50,000 BP (Table 3). At the 2σ limit, the difference between the uncorrected IsoTrace results and those for the GSC background materials agrees with the 0.2 pMC limit. Therefore, the IsoTrace results, corrected by the background results of Table 1, indicate that these samples are actually 41,000 – 46,000 BP instead of > 50,000 BP, as quoted by the GSC. It is to be expected that many radiocarbon dating facilities, which have not checked the intrinsic ^{14}C content of their background material, are also quoting ages older than the actual ages.

TABLE 2
Re-analysis of the background samples from the Geological Survey of Canada

Sample treatment	Material	^{14}C content (pMC)	Apparent age (yr BP)
Acid hydrolysis	Calcite	0.54 ± 0.04	42,000 ± 600
Combustion	Anthracite	0.36 ± 0.03	45,200 ± 700

TABLE 3
Intercomparison with the Geological Survey of Canada

Wood sample	
GSC measurement	< 0.20 pMC
IsoTrace measurement	0.46 ± 0.03 pMC
GSC anthracite	0.36 ± 0.03 pMC
Difference	0.10 ± 0.04 pMC
Shell sample	
GSC measurement	< 0.20 pMC
IsoTrace measurement	0.65 ± 0.04 pMC
GSC calcite	0.54 ± 0.04 pMC
Difference	0.11 ± 0.06 pMC

HIGH-PRECISION INTERCOMPARISON WITH THE QUATERNARY RESEARCH CENTER OF THE UNIVERSITY OF WASHINGTON

The radiocarbon facility at QRC regularly dates samples to a precision of better than 0.2% and has a proven dating capability to > 65,000 BP. Their contamination due to sample preparation has been carefully checked using a ^{14}C enrichment process. Thus, QRC is an ideal partner for intercomparison checks. I divided this intercomparison study into three analytical stages:

1. Comparison of NBS I oxalic acid standards
2. Comparison of pretreated samples, submitted as CO_2
3. Comparison of untreated samples.

The results of the first two stages are presented below.

Comparison of NBS Standards. As all sample ages are obtained by comparing their ^{14}C content to standards, this is the logical place to start. I do not actually prepare NBS oxalic acid standards at IsoTrace. They are prepared at the United States Geological Survey (USGS) as acetylene. This acetylene is then graphitized at the IsoTrace laboratory. I compared these standards with standards prepared from CO_2 supplied by QRC. The ratio of the IsoTrace standard to the QRC standard was 0.9992 ± 0.0020, giving the IsoTrace standard a clean bill of health.

Comparison of Pretreated Samples. For this stage, Minze Stuiver selected three samples of widely varying ages, which had been analyzed previously to high precision by QRC. The samples were supplied as CO_2. To ensure a true blind test, the QRC ages were not made available until after I reported my results. Table 4 shows the uncorrected and background-corrected results of this intercomparison. It is unusual for a decay-counting laboratory to show uncorrected results because background subtraction is integral to their procedures. AMS laboratories frequently do show uncorrected results as the effect of the correction is negligible, in most cases. A background-corrected AMS date is recalculated after subtracting the blank correction from the results for the sample as well as the results for the standards used. I used the measured upper limit for the contamination by the IsoTrace graphitization process of 0.077 ± 0.005 pMC as an estimate for the background correction factor. The agreement at this level of precision is quite satisfactory and the comparison shows no statistically significant offsets.

TABLE 4
High-precision intercomparison with the Quaternary Research Center (QRC)

QRC results		IsoTrace results		
Lab no.	Age (yr BP)	No. of samples analyzed	Uncorrected age (yr BP)	Background corrected age (yr BP)
QL-11288	4132 ± 18	18	4149 ± 21	4157 ± 21
QL-11312	6973 ± 20	16	7002 ± 20	7019 ± 20
QL-1787	> 55,000	16	49,550 ± 340	53,100 ± 600

CONCLUSION

Stage 3, the analysis of the untreated samples, is currently underway. Comparison of these results with the Stage 2 results will allow a better estimate of the upper limit for the contamination by the combustion process.

Over the years, many "very old" samples, which had never actually been measured, have been submitted to our laboratory. I think it is prudent to distrust such samples until they have been measured, as most samples, to a certain extent, appear to be contaminated.

Finally, it is quite surprising that old samples have never been included in international intercomparisons. I believe that this is a major oversight as many of the participating laboratories claim to date samples older than 35,000 BP.

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