INTERCOMPARISON OF HIGH-PRECISION $\Delta^{14}C$ ANALYSES USING GAS COUNTING AND AMS

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ABSTRACT. We report results of a three-year intercomparison experiment between the WHOI Radiocarbon Laboratory (now at University of California, Irvine) and the NSF-University of Arizona AMS Laboratory. The purpose of this study was to compare high-precision measurements of samples obtained routinely using gas proportional counting techniques with results obtained using AMS techniques. Three sets of annually banded, modern coral samples were used for the intercomparison. Each sample was acidified to CO_2 at WHOI and split into two fractions. The larger fraction was converted to acetylene gas and counted at WHOI in quartz, gas-proportional beta counters. The smaller fractions were converted to graphite and analyzed for ^{14}C using AMS techniques at the University of Arizona. Results of the three sample sets are presented. Except for a single outlier, the data from the two laboratories are in good agreement. Of the 13 samples in the third set of the intercomparison, for which a new high-intensity ion source was in operation at the Arizona AMS laboratory, agreement of results is excellent. This finding indicates that measurements made with precisions of < 3‰ are reproducible at both laboratories.

INTRODUCTION

High-precision ^{14}C analyses are required in several areas of geophysics. Examples of such data sets include tree rings and annually banded corals. This is due to the small $\Delta^{14}C$ variations that were present in atmospheric and oceanic carbon pools during the pre-bomb period.

Only a few laboratories in the world are capable of high-precision ^{14}C measurements. Most use β counting methods to measure the decay of ^{14}C, that is, gas proportional counting (Stuiver and Quay 1980) and liquid scintillation counting (Pearson *et al.* 1986) techniques. Such precise measurements are difficult to attain, as they require large sample sizes and/or long counting periods. These problems set limitations on the number of analyses that can be made, and thus, the number of high-precision ^{14}C analyses reported in the literature is relatively few in comparison with lower precision analyses.

We report here an intercomparison of high-precision ^{14}C measurements obtained using β and accelerator mass spectrometry (AMS) techniques. We define high-precision as a total uncertainty (statistical plus laboratory uncertainty) of <3‰. Jones *et al.* (1994) recently published AMS measurements of duplicate seawater dissolved inorganic carbon (DIC) samples with statistical uncertainties that ranged from ± 2.3 to 9.7‰. However, they made no independent measurements of their samples using β-counting techniques.

METHODS

All 30 of the samples used for the intercomparison were coral bands cored from a single coral colony at Abraham Reef, Great Barrier Reef, Australia (22°S, 159°E). Two cores were taken from the top of the 8-m-high colony of *Porites australiensus*; the first core was drilled in December 1985 and the second in May 1991. Methods used to clean, X-ray and section the coral were reported previously (Druffel and Griffin 1993; Griffin and Druffel 1985).

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Bi-annual coral bands were taken from the core collected in 1985 and used for the first and second phases of the intercomparison. Annual coral bands from the post-bomb period (post-1958) were obtained from the 1991 core for the third phase of our experiment.

Ca. 25 g of coral (aragonite, a crystalline form of calcium carbonate) were acidified to produce 5 liters of CO_2 gas. Each gas sample was split into two fractions: 1) a 5.0-liter CO_2 subsample for gas-counting analyses; and 2) a 10-ml CO_2 subsample for AMS analyses.

At Woods Hole Oceanographic Institution (WHOI), the 5-liter samples were converted to acetylene gas via a lithium-carbide intermediate, and purified through charcoal at 0°C. Each sample was counted for 6–7 2-day periods in 1.5-liter quartz, gas-proportional β counters according to standard procedures (Griffin and Druffel 1985). At the University of Arizona, the 10-ml samples were split into four equal volumes and converted to graphite according to standard methods (Slota *et al.* 1987). Four or five targets were measured for each sample using AMS techniques (Donahue, Jull and Toolin 1990).

RESULTS

[14]C results for the 30 coral samples are reported as fraction of modern (F) in Table 1 for both β and AMS analyses. Age-corrected $\Delta^{14}C$ results for the first 17 samples obtained by β techniques were published previously (Druffel and Griffin 1993). Errors reported for the β measurements include both counting statistics and laboratory reproducibility error. The average statistical counting uncertainty of each analysis is ±2.1‰, and includes background and standard (HOxI) measurement uncertainties and the $\delta^{13}C$ correction. The laboratory reproducibility uncertainty was determined from multiple, high-precision analyses of a modern coral standard. The standard deviation of 10 results was 3.0‰; thus, the laboratory uncertainty constituted *ca.* 40% additional error. Hence, to obtain our total uncertainty on samples with similar statistical uncertainty (*i.e.*, ± 2.1‰), we multiply the statistical uncertainty by 1.4. The $\delta^{13}C$ values measured on the reburned acetylene gas were used to correct the β and AMS F results. All $\delta^{13}C$ results used for this study were performed at WHOI on a VG Micromass 602E isotope ratio mass spectrometer.

The AMS results are the weighted averages of 4 or 5 independent measurements on each sample. The uncertainties on the individual measurements were a quadratic combination of *ca.* 4‰ counting statistical uncertainties and an assigned 4‰ instrument random uncertainty (Donahue, Jull and Toolin 1990). The second-to-last column in Table 1 is the ratio, $R_{[beta/AMS]}$, of the β and AMS F measurements. The results in this column show that, except for one outlier, the agreement of results from the two laboratories over the entire period of the intercomparison is satisfactory (Fig. 1). The reason for the result for sample 13 is not known, but it is >7 standard deviations from the average of all the measurements of the ratio, and is clearly not statistical. If this one result is eliminated from the calculation, the other 29 ratios have a weighted average

$$< R_{[beta/AMS]} >_{wtd\ avg} = 0.99980 \pm 0.00079 . \tag{1}$$

The uncertainty quoted is the standard deviation of the average, obtained from the statistical uncertainties of the individual measurements. The "external uncertainty" obtained from the scatter of individual measurements about the average, from the equation

$$\sigma_{scatter} = [(\textstyle\sum_i (\chi - \chi_i)^2) / (N(N-1))]^{1/2} = 0.00101 . \tag{2}$$

That is, $\sigma_{scatter} = 1.28\ \sigma_{statistical}$.

TABLE 1. Results of high-precision ^{14}C measurements made at the WHOI (F_{beta}) and Arizona (F_{AMS}) laboratories using beta counting and AMS techniques, respectively. The ratio of F_{beta}/F_{AMS}, or $R_{[beta/AMS]}$ and resultant uncertainties for each sample appear in the last two columns.

Year measured	Sample no.	F_{beta}	F_{beta} uncert.	F_{AMS}	F_{AMS} uncert.	R F_{beta}/F_{AMS}	R
1990–91	1	.94157	.0030	.93476	.0027	1.00729	.00433
	2	.92971	.0026	.93773	.0030	.99145	.00421
	3	.94242	.0030	.94610	.0025	.99611	.00412
	4	.93838	.0029	.94037	.0025	.99788	.00407
	5	.93282	.0029	.93218	.0025	1.00069	.00411
	6	.92883	.0028	.93023	.0029	.99849	.00433
	7	.92953	.0029	.93497	.0029	.99418	.00437
	8	.92425	.0030	.91011	.0028	1.01553	.00454
	9	.92924	.0029	.93343	.0029	.99551	.00438
	10	.93843	.0026	.94234	.0025	.99585	.00382
	11	.94342	.0028	.94625	.0031	.99702	.00441
1991–92	12	.94777	.0029	.95108	.0050	.99652	.00606
	13	.93761	.0026	.90845	.0030	1.03210	.00445
	14	.94146	.0028	.94643	.0040	.99474	.00514
	15	.94032	.0030	.93124	.0030	1.00975	.00458
	16	.92346	.0028	.92156	.0030	1.00206	.00446
	17	.92410	.0030	.93089	.0040	.99270	.00535
1993	18	1.12456	.0029	1.12500	.0028	.99961	.00358
	19	1.13968	.0054	1.13280	.0032	1.00607	.00555
	20	1.13547	.0030	1.13010	.0035	1.00475	.00409
	21	1.12768	.0038	1.1206.ð	.0035	1.00632	.00462
	22	1.12801	.0030	1.13370	.0032	.99498	.00386
	23	1.13289	.0030	1.13190	.0035	1.00088	.00407
	24	1.07129	.0029	1.07370	.0031	.99776	.00395
	25	1.12449	.0032	1.12480	.0033	.99973	.00409
	26	1.09701	.0035	1.09320	.0029	1.00348	.00416
	27	1.12637	.0032	1.13070	.0029	.99617	.00381
	28	1.13071	.0029	1.13350	.0035	.99754	.00400
	29	1.10417	.0029	1.10430	.0033	.99988	.00398
	30	1.11546	.0029	1.11350	.0029	1.00176	.00369

It is interesting to note that the final 13 measurements in Table 1 were made in 1993, after a new high-intensity ion source had been installed on the Arizona AMS instrument. For these final 13 measurements

$$< R_{[beta/AMS]} >_{wtd\ avg} = 1.00070 \pm .00112 \qquad (3)$$

where the uncertainty is derived from individual uncertainties, and

$$\sigma_{scatter} = 0.90\ \sigma_{statistical}\ . \qquad (4)$$

This shows that for the last 13 measurements, there is no statistical difference at the 1‰ level between the two laboratories.
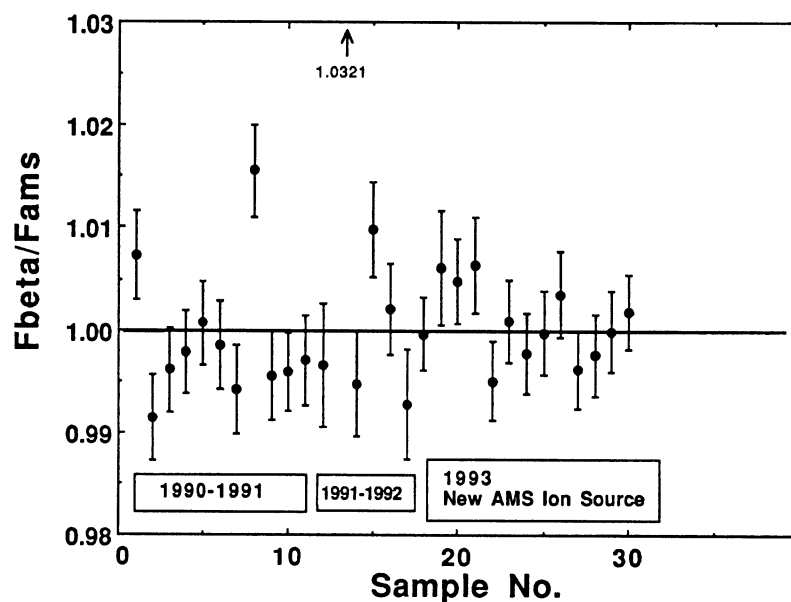
Fig. 1. Ratio of F_{beta}/F_{AMS} ($R_{[beta/AMS]}$) in 30 samples measured during the intercomparison period 1990–1993. Note that the new high-intensity ion source was in operation at the AMS during the measurement of the last 13 samples.

CONCLUSION

Our results indicate that the Arizona AMS laboratory can produce reliable results on modern materials with standard deviations of *ca.* 3‰, comparable with precisions obtained by β counting at the WHOI (now UC Irvine) laboratory. The AMS results require 2–4 mg of carbon and an instrument time of *ca.* 2 h.

This finding holds great potential for various fields of geophysics that require high-precision ^{14}C measurements. The throughput of samples that can be measured with high precision will increase, and hence, change the approaches and types of problems that can be tackled as we unravel the mysteries of the carbon cycle. Examples include the accurate measurement of seasonal trends in $\Delta^{14}C$ over the past centuries in tree rings and corals, and small deep-sea corals that grow at very low rates.

ACKNOWLEDGMENTS

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