ACCURACY AND PRECISION IN DATING MICROGRAM CARBON SAMPLES

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ABSTRACT. The accuracy of AMS radiocarbon determinations on very small samples has been tested by measuring a suite of microgram-sized samples of a known-age material. The total measurement precision for the smallest sample (50μg) was found to be ±3% and the precision improved with larger sample size. The accuracies of the measurements were found to be within the measurement precisions.

Accelerator mass spectrometry (AMS) made possible the radiocarbon dating of samples containing only milligrams of carbon. As could be expected, pressure to develop methods for dating smaller amounts of carbon continued after the advent of AMS. We showed in 1986 that it was possible to date a 50μg sample of carbon using AMS to a precision which was not limited by the counting statistics of the measurement (Nelson *et al*, 1986b). We found that our total measurement system, from isolation of the carbon as CO_2 to final direct counting of the ^{14}C, was ca 1% efficient. Hence, it should be possible to measure the concentration of a modern sample to a counting-statistics precision of 1% using as little as 17μg of carbon. However, the graphite which is finally measured by AMS includes an unknown amount of ^{14}C which is introduced into the sample during processing. We researched the contribution of contamination to processing (Vogel, Nelson & Southon, 1987) and demonstrated that this places a limit on the ultimate precision possible in measuring very small samples. Since then, we have made use of samples containing 20–500μg of carbon in numerous studies in archaeology (Snow *et al*, 1986; Nelson *et al*, 1986a), paleo-climate (Peteet *et al*, ms), atmospheric science (Wahlen *et al*, ms), oceanography (Pedersen, Vogel & Southon, 1986), earth science (Vogel *et al*, 1989), and ecology (Bauer, Spies & Vogel, ms). We present here evidence that our measurement system can not only produce precise dates from very small amounts of materials, but that these dates are also accurate.

We tested our AMS system by dating several aliquots of an extracted cellulose provided by the Quaternary Isotope Lab of the University of Washington (Archaeology Comparison Test sample number 1, or ACT-1). These were processed in our usual manner as described in Vogel, Neslon and Southon (1987). The aliquots varied in size from 50 ± 4μg C to 6490 ± 4μg C (Table 1), as measured manometrically after combustion to CO_2 in sealed quartz tubes using CuO oxidant. These samples were processed without dilution by ^{14}C-free CO_2 as has been done by others (Verkouteren *et al*, 1987). The CO_2 was reduced to a filamentous graphite coating on cobalt powder using hydrogen in our usual reactors. The two largest CO_2 samples were divided and graphitized in 3 and 4 reactors, respectively, since each reactor is limited to a maximum of 2 mg of carbon. Most contamination arises from combustion (Vogel, Nelson, and Southon 1987), and graphitisation does not result in large isotope fractionation (Vogel,

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TABLE 1

14C concentrations and measurement parameters for various-sized samples

Size* (μgC)	12C⁻ (μA)**	N meas	Time (sec)	Total counts	Graphite†		14C concentrations				Precision§ %	Accuracy# %
							Bgnd‡		Sample			
					(pMC)	±	(pMC)	±	(pMC)	±		
50	11.6	3	600	12424	75.64	0.95	3.00	2.00	72.64	2.21	3.0	2.2
90	14.0	4	800	20284	74.98	0.93	1.67	1.11	73.31	1.45	2.0	1.3
175	18.2	4	1000	33180	74.68	0.66	0.86	0.57	73.83	0.87	1.2	0.6
260	18.3	3	600	20194	75.35	0.78	0.58	0.38	74.78	0.87	1.2	0.7
420	22.7	4	800	33178	74.32	0.70	0.35	0.15	73.97	0.72	1.0	0.4
840	20.6	7	1600	60877	76.77	0.69	0.35	0.15	76.42	0.71	0.9	2.9
4700	23.3	22	3700	153373	74.42	0.46	0.35	0.15	74.13	0.47	0.6	0.2
6490	22.4	24	5100	202405	74.50	0.24	0.35	0.15	74.14	0.26	0.4	0.2

*Amount of CO_2 from combustion. Two largest samples analyzed using 4 separate aliquots of prepared graphite.

**Current is the average for the total time of the N measurements.

†14C concentration calculated from the measured $^{14}C/^{13}C$ ratio using the measured δ ^{13}C value of $-20.5‰$. Final concentrations corrected to a δ ^{13}C of $-25‰$.

‡Background calculated as $(1.5 \pm 1.0 \mu g$ modern equivalent) divided by the sample size in μg. Large sample ($>400\mu g$) background was 0.35 ± 0.15 pMC.

§Precision is the quadratic combination of the uncertainty in the background and the standard deviation of the set of N measurements.

#Accuracy calculated as the percentage difference from the value determined by a high-precision counting lab. The material was ACT-1 cellulose provided by M Stuiver (A = 74.27 ± 0.18 pMC, 2390 ± 20 BP).

Southon & Nelson 1987). Thus, the graphite from the separate reactions of the large samples was mixed and then considered as a single quantity. The cobalt powder to carbon weight ratios ranged from 15 for the smallest sample to 3 for the larger ones. This variation does not affect these measurements to the desired precision (Vogel, Southon & Nelson, 1987). No special handling (*ie*, argon atmosphere or closed systems) was used, despite the known presence of a "hot," organic, airborne contaminant. (Spent biomedical scintillants are stored in a room below our laboratory.)

Portions containing $300–500\mu g$ carbon of the large graphites were pressed into individual sample holders for measurement. The smaller samples were pressed into identical holders above a layer of pure silver powder so that all samples were recessed in the holes by a similar distance. The ion currents from these smaller samples were initially more than half the current from the larger samples, as is expected solely from carbon dilution by the cobalt (Vogel, Southon & Nelson, 1987). Once the relatively thin layer of graphite/cobalt over the silver base was sputtered through for the smallest samples, the ion output decreased with time. The beam shape also changed to that of a "doughnut," causing differential transmission effects between the ^{14}C and the ^{13}C. This was observed for only the $50\mu g$ sample, the $^{14}C/^{13}C$ ratio of which abruptly changed by 5% after 10 minutes of measurement. Even so, the 10 minutes of usable beam produced over 12,000 counts of ^{14}C, a total system efficiency of 0.6% from CO_2 to counted ^{14}C.

Table 1 gives the ^{14}C concentration results for the 8 sample sizes. The total measurement times and the total ^{14}C counts refer to the sum of all the measurements on each sample. No measurement was limited by statistics by >0.9%. The ^{14}C concentrations of the graphites are given in percent modern carbon (pMC), and the quoted uncertainties are the observed reproducibility (at 1σ) of the 3 to 24 different measurements made on each graphite sample. These isotope ratios were measured to precisions between 0.4 and 1.3%. The method for determining the background to be subtracted from these measured concentrations was discussed in Vogel, Nelson and Southon (1987). However, since that publication, we have taken steps to reduce our processing contamination. Our background has been reduced from the 0.48 ± 0.16pMC reported for large coal samples to 0.35 ± 0.15pMC as measured on amber and 45Myr (sic!) wood. The small sample background is now calculated to arise from 1.5 ± $1.0\mu g$ C modern-equivalent contamination during processing. This value was used to calculate the background subtracted from these small samples. We attribute our improvements to using cobalt rather than iron catalyst (Vogel, Southon & Nelson, 1987) and to storing our quartz combustion tubes in water vapor prior to use to dislodge adsorbed CO_2 (Zumbrunn, Neftel & Oeschger, 1982). The resultant final sample ^{14}C concentrations are shown in Table 1 and Figure 1. The total measurement precision for the sample includes the precision of the graphite measurement and the background uncertainty. This precision, in percent form, ranged from 3.0% for the $50\mu g$ sample to 0.4% for the largest sample.

An indication of the accuracy (in distinction to the precision) of these measurements is found by comparing them to the value obtained by the
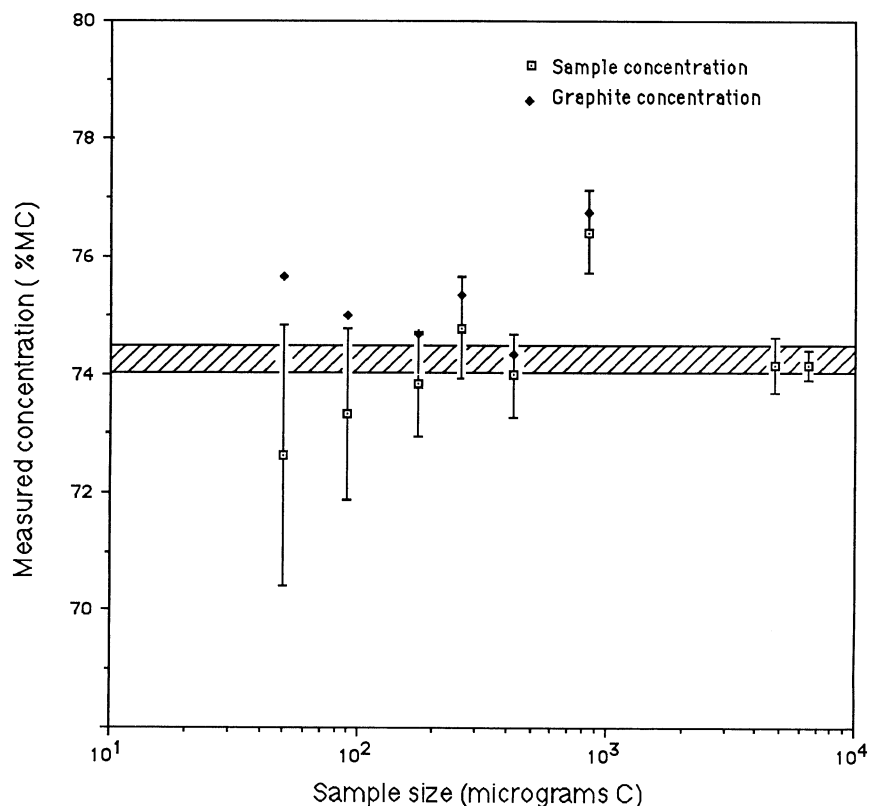
Fig 1. ^{14}C concentration *vs* processing size for 8 samples of ACT-1 cellulose. The 1σ width obtained by the University of Washington Quaternary Isotope Lab is shown as the hatched bar (74.27 ± 0.18 pMC, 2390 ± 20 yr BP). The graphite ^{14}C concentration, without any background subtraction, is also shown for the 6 smaller samples.

laboratory that provided the test material. Stuiver (pers commun, 1988) has determined this material to have an activity of 74.27 ± 0.18 pMC, corresponding to an age of 2390 ± 20 BP. The weighted average for all determinations in this test is 74.30 ± 0.19 pMC, or 2386 ± 20 BP. The very good agreement indicates that, on average, our results are accurate within our stated measurement precision.

However, it is the accuracy of individual determinations, and the effect of sample size on accuracy that is of greatest interest. The relative differences between our determinations and that of Stuiver are given in the last column of Table 1. With one exception, these differences are all smaller than the measurement precisions, indicating that our quoted uncertainties may be too conservative. An examination of the data suggests that we have over-estimated the uncertainty of the measurement background. However, given the very small amounts of contaminating material involved, we believe this caution is justified. A very large amount of experience on ultra-

small samples will be required before we can predict with confidence that processing contamination varies by $<1\mu g$ C. The single sample that is apparently discrepant is large ($840\mu g$ C) and is 3σ away from the mean, which would not be statistically unusual for this number of determinations. A later remeasurement of the remaining graphite from this sample gave a concentration of 74.33 ± 0.97pMC. The error in the initial determination probably arose from sample presentation in the ion source and was not inherent to the graphite. Even with this possible outlier, the spread of results is about that expected for replicative determinations on a single sample:

$$(\chi^2 = 11.3 < \chi^2_{.05} = 14.07; n = 8).$$

The results for the smallest aliquots are accurate within their measurement precisions. While the measurements for the small samples are not as precise as those for the larger samples, there is no bias in the results obtained: measurement accuracy reflects measurement precision. It is clear that, with the methods used here, reliable ^{14}C determinations can be directly made on samples containing only a few tens of micrograms of carbon.

REFERENCES

Bauer, J E, Spies, R B, Vogel, J S, ms, Fossil carbon cycling in hydrocarbon seep sediments: ^{14}C abundances in organic, inorganic and faunal carbon: Ms in preparation.
Nelson, D E, Loy, T. H, Vogel, J S and Southon, J R, 1986a, Radiocarbon dating blood residues on prehistoric stone tools: Radiocarbon, v 28, no. 1, p 170–174.
Nelson, D E, Vogel, J S, Southon, J R, and Brown, T A, 1986b, Accelerator radiocarbon dating at SFU, *in*, Stuiver, M, and Kra, R S, Internatl ^{14}C conf, 12th, Proc: Radiocarbon, v 28, no. 2A, p 215–222.
Pedersen, T F, Vogel, J S and Southon, J R, Southon, 1986, Copper and manganese in hemipelagic sediments at 21 deg N, east Pacific rise: diagenetic contrasts: Geochim et Cosmochim Acta, v 50, p 2019–2031.
Peteet, D M, Vogel, J S, Nelson, D E, Southon, J R, Nickman, R J and Heusser, L E, ms, AMS ^{14}C dating of macrofossils indicates presence of Younger Dryas climatic reversal in northeastern USA: Ms subm to Quaternary Research.
Snow, B E, Shutler, R, Jr, Nelson, D E, Vogel, J S and Southon, J R, 1986, Evidence of early rice cultivation in the Phillipines: Phillipine Quarterly Culture & Soc; v 14, p 3–11.
Verkouteren, R M, Klouda, G A, Currie, L A, Donahue, D J, Jull, A J T and Linick, T W, 1987, Preparation of microgram samples on iron wool for radiocarbon analysis via accelerator mass spectrometry: a closed system approach: Nuclear instruments & Methods, v B29, p 41–44.
Vogel, J S, Briskin, M, Nelson, D E and Southon, J R, 1989, Ultra-small carbon samples and the dating of sediments, *in* Long, A and Kra, R S, eds, Internatl ^{14}C conf, 13th, Proc: Radiocarbon, v 31, no. 3, in press.
Vogel, J S, Nelson, D E and Southon, J R, 1987, ^{14}C background levels in an accelerator mass spectrometry system: Radiocarbon, v 29, no. 3, p 323–333.
Vogel, J S, Southon, J R and Nelson, D E, 1987, Catalyst and binder effects in the use of filamentous graphite for AMS: Nuclear Instruments & Methods, v B29, p 50–56.
Wahlen, M, Tanaka N, Henry, R, Deck, B, Zeglen J, Vogel J S, Southon, J, Shemesh, A, Fairbanks R and Broecker, W, ms, ^{14}C in methane sources and in atmospheric methane: The contribution from fossil carbon: Ms subm to Science.
Zumbrunn, R, Neftel, A Oeschger, H, 1982, CO_2 measurements on 1cc ice samples with an IR laserspectrometer (IRLS) combined with a new dry extraction device: Earth Planetary Sci Letters, v 60, p 318–324.