^{14}C BACKGROUND LEVELS IN AN ACCELERATOR MASS SPECTROMETRY SYSTEM

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ABSTRACT. The levels and sources of the measurement background in an AMS ^{14}C dating system have been studied in detail. The relative contributions to the total background from combustion, graphitization, storage, handling, and from the accelerator were determined by measuring the ^{14}C concentrations in samples of anthracite coal ranging in size from 15μg to 20mg. The results show that, for the present system, the uncertainty in the background is greater than that due to measurement precision alone for very old or for very small samples. While samples containing 100μg of carbon can yield useful ^{14}C dates throughout the Holocene, 200 to 500μg are required for dating late Pleistocene materials. With the identification of the procedures that introduce contamination, the level and uncertainty of the total system background should both be reducible to the point that 100μg of carbon would be sufficient for dating most materials.

INTRODUCTION

The efficiency of accelerator mass spectrometry (AMS) for the direct counting of radioisotopes has greatly reduced the sample sizes required for obtaining ^{14}C ages. In our system, the total detection efficiency is ca 1%, inclusive of all steps from isolating the carbon as CO_2 to the detection of the accelerated ^{14}C ions (Nelson *et al*, 1986). In principle, this efficiency is sufficient to allow measurement of samples containing only a few tens of micrograms of carbon without placing serious counting statistical limitations on the measurement uncertainty. For example, with 1% efficiency, only 40μg of 6000-year-old carbon are required to provide 1% counting statistics.

The capability to analyze such small samples will clearly be useful in a number of disciplines, and appropriate methods for doing so must be developed and tested. We have found that the catalytic graphitization of CO_2 onto an iron powder substrate (Vogel *et al*, 1984) can provide graphite specimens suitable for analysis from samples containing as little as 15μg of carbon. However, for such small samples, the possibilities of contamination are proportionately greater than for large samples. This means that the contributions to the background from the entire measurement process must be carefully examined.

The background level for an AMS-determined ^{14}C concentration has three components: 1) the contamination of the sample *in situ* before selection, 2) the contamination of the sample during preparation, and 3) the machine or detection background. The problems in 1) are dependent on the sample and the methods of purification used to isolate the carbon of interest, and are not discussed further here. In this study, we have evaluated the amounts and the sources of contaminants introduced in burning the samples to CO_2 and in producing the graphite specimens for analysis. We have also estimated the contribution to the background from the accelerator system. For very small samples, we find that the background becomes the dominant portion of the final age uncertainty.

[1] Vycor Laboratory Glassware, Corning Glass Works, Corning, New York

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TECHNIQUE

The contributions to the background were determined by preparing and measuring the ^{14}C concentration of ^{14}C-free material in exactly the same manner as was used for all other samples. The material used was anthracite coal (obtained from a deep mine in Pennsylvania) which had been pulverized and processed through the standard acid/base washes (Nelson & Hobson, 1982). This anthracite powder received occasional further acid rinses to desorb any atmospheric CO_2. For combustion to CO_2, the pretreated samples were sealed in evacuated 7mm diameter Vycor[1] tubes along with 0.25 to 1g of wire-form copper oxide. Both the Vycor tubes and the copper oxide used in the combustion were heated in air to 900° C prior to use in order to assure that any surface carbon was oxidized. A group of ten loaded tubes was placed in a muffle furnace heated to 900° C and held at that temperature for 1/2 to 1 hour.

The resulting CO_2 was processed in our graphitization apparatus shown in Figure 1. The Vycor tubes were broken inside a bellows and the CO_2 collected in a small (5.8ml) volume equipped with a solid-state pressure transducer for measuring the quantity of gas. The CO_2 was then transferred to one of the four reaction vessels, where the iron catalyst had already been re-reduced in hydrogen. The usual catalyst iron was 99% pure, spherical, -200 mesh powder. An amount of ultra-pure hydrogen in excess of the stoichiometric amount needed for complete reduction was added to the sample CO_2. An oven at ca 650° C was placed around the catalyst end of the reactor while a cold finger was placed at the other end to trap the water resulting from the reaction. Two graphitizations per reactor per day were possible. The resultant graphite-coated iron powder was stored in small glass bottles until needed. For measurement, the graphite on iron was pressed into 1.1mm diameter dimples in aluminum sample holders. For "large" samples, 200 to 400μg of carbon were used in a single sample holder. Ultra-small samples ($<100\mu$g) were placed on a bed of silver in the dimple before being pressed.

The ^{14}C and ^{13}C extracted from the samples were simultaneously accelerated and detected in a continuous dual beam mode as described in Nelson *et al* (1984, 1986). Negative carbon ion beams of up to 55μa were obtainable on some days, but the usual ion source output was more often 20 to 40μa. All measurements were obtained with respect to identically prepared samples of the NBS oxalic acid standard for which the ^{14}C count rates were typically 50 to 75 per second. Most of the anthracite sample measurements consisted of three 20-minute 'runs.' These runs were performed over a period of 8 to 12 hours along with the other samples in the 20-sample wheel.

MACHINE BACKGROUND

The background level due to the accelerator system should be low, as the ion identification technique of AMS implies a low probability of mis-
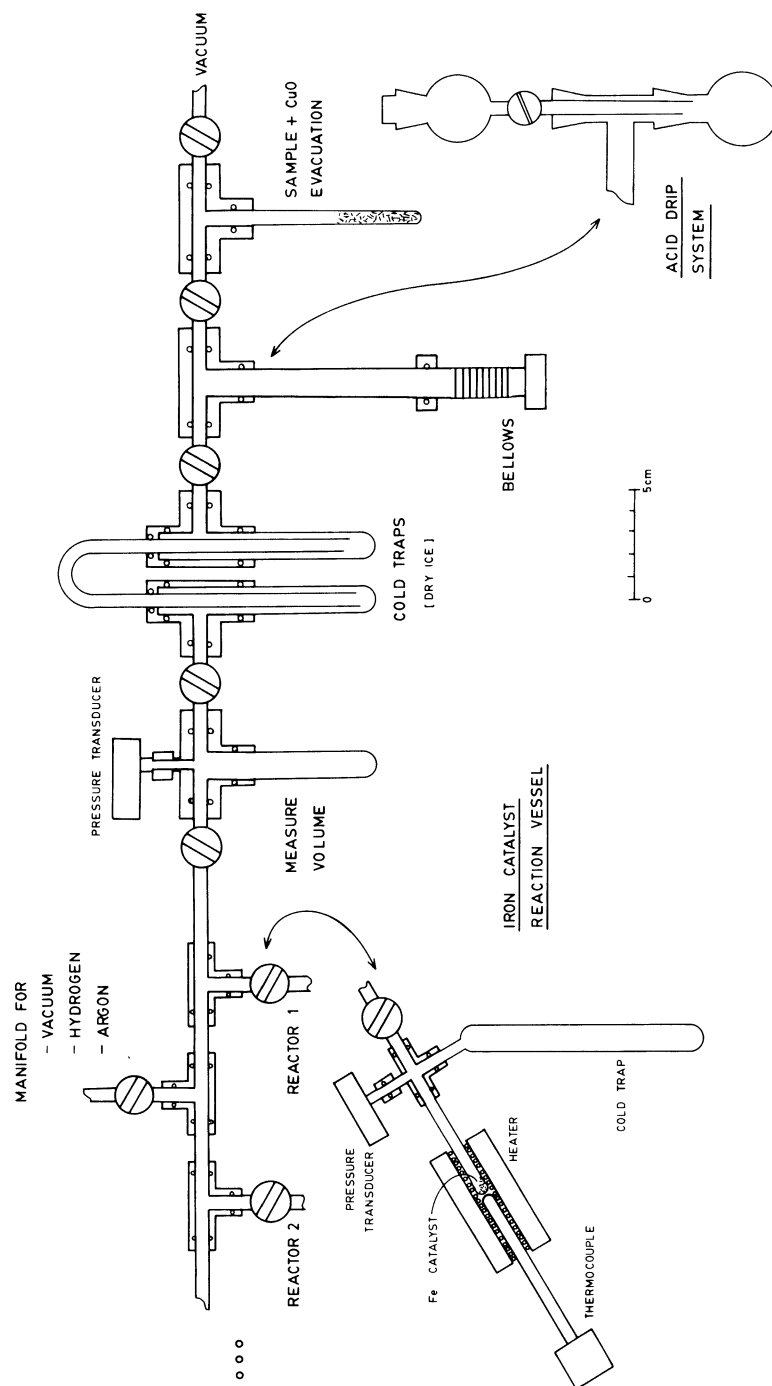
Fig 1. Multiple reactor apparatus for the graphitization of CO_2 over an iron powder catalyst. The volume of the reaction vessels could be varied by using different sized cold traps. Reaction volumes as small as 3ml were possible.

taking other ions for ^{14}C. Only ^{14}C or specially scattered ^{13}C could be counted as sample ^{14}C, and all other ions were easily separated in the filtering system. The level of this machine background would be best found by using a natural graphite which needed no sample preparation and which was known to have absolutely no ^{14}C concentration. Since we did not have access to graphite which is known to be free of ^{14}C, we have used spectroscopic graphite of unknown provenance as well as graphite which we produced from old materials of well known ages to estimate our machine background.

In our system, up to 750nA of $^{13}C^{4+}$ have been analyzed simultaneously with the ^{14}C, and scattered ^{13}C could be expected to be a serious background problem. However, measurements showed that the contribution from this source was equivalent to a ^{14}C age of ca 60 to 65 kyr (ca 0.04% modern). The major component of the background was real ^{14}C. This contaminant ^{14}C must be inherent to the graphite, be added during handling, or come from portions of the ion source other than the sample material. Although we could not distinguish which of these three was responsible for our machine background, sample cross-talk in the ion source was discounted by measuring the ^{14}C concentration of a small anthracite sample which was placed next to the NBS oxalic acid standard in the sample wheel. The sample did not increase its ^{14}C concentration during the measurement program, but displayed the usual decrease in concentration as the surface contaminant layer was sputtered away. This surface contamination was observed on many anthracite samples and appeared to be an artifact of the pressing. A comparison of the machine background derived from the unprocessed graphite with the total system background obtained from large samples of processed old materials is presented in Table 1. We have assumed that our machine background was ca 55 kyr.

PREPARATION CONTAMINATION

We measured the contamination arising in each step of the preparation process as listed in Table 2 by varying the amounts of carbon used in

TABLE 1
Estimation of machine background

Material	Measured activity	Derived machine background	Equivalent age BP
Graphite*	0.00128 ± 0.00056	—	53.5 kyr
Best graphitized anthracite	0.00142 ± 0.00023	—	52.7
Graphitized calcite**	0.00125 ± 0.00060	—	53.6
Graphitized 58 kyr wood†	0.00155 ± 0.00012	0.00089	56.4
Graphitized 45 kyr wood‡	0.00446 ± 0.00030	0.00081	57.2

* Graphite rod of unknown provenance
** Icelandic doublespar
† QL-195
‡ QL-1543, SFU-TO2

TABLE 2

Sources and contributions of contamination in sub-milligram
AMS carbon samples

Type of contamination	Carbon source	Measured contribution	
Combustion	Adsorbed gas on Vycor	1.5 ± 1.0	μg mod
	C in CuO	<0.5	μg mod
Graphitization	Memory effect	0.36 ± 0.19	μg mod
	C in Fe catalyst	<0.1	% mod
Storage	Adsorbed $CO2$	<0.2	μg mod
Handling	CO_2/'dirt'	<0.1	μg mod
Total	—	2.2 ± 1.1	μg mod

the individual steps and by determining the ^{14}C content of the resulting graphite. While contamination could result from the inclusion of carbon of any age, we made the assumption that most of the extraneous carbon would come from dirt or adsorbed gases having an essentially modern age. Some contribution of dead carbon could be expected from chemicals and catalysts used in the processing; but small amounts of old carbon negligibly affect the ^{14}C concentration determination. Hence, contamination will be discussed as an equivalent amount of modern material added to the anthracite samples. For the small anthracite samples discussed here, the measured ^{14}C concentration was considerably more than the machine background and we made the approximation that the measured ^{14}C was due entirely to the contamination of the sample.

The variation in total system background with sample size is plotted in Figure 2 for amounts of carbon from 10μg to 20mg. For anthracite samples of <300μg, the data represent one ^{14}C concentration determination. The larger samples have two or more measurements for each with only the average value plotted here. Two trends were evident in the data: a constant level of ^{14}C concentration for samples >500μg and a linear inverse relation to sample size for smaller pieces of anthracite.

The total system background concentration for large samples was, on average, 0.48 ± 0.16% modern (equivalent to 43 kyr ^{14}C age) and did not vary with sample size. The anthracite we were using must have become contaminated through handling or pretreatment before combustion. This conclusion was further supported by the background levels measured for geologic calcite and those determined by inference from known-age wood, as shown in Table 1. The source of this coal contaminant is still under investigation, and we speculate that standard pretreatment procedures may not be adequate for coal to be used as a background material for AMS ^{14}C determinations.

For samples <500μg, the total system background behaved as if the samples were contaminated with a constant amount of modern material. The best fit of the data to a linear inverse mass relation showed that total contamination equivalent to $2.2 \pm 1.1\mu$g of modern material was added during processing. The sample processing was then carefully analyzed to determine the contributions of each procedure to this total system background.
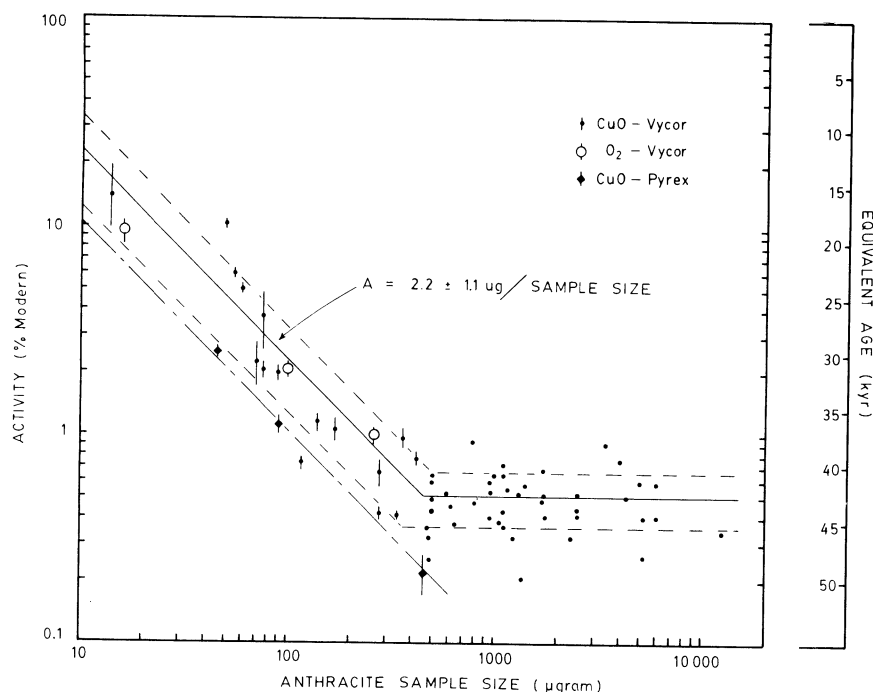
Fig 2. The total system background expressed as a ^{14}C concentration *vs* anthracite sample weight from $10\mu g$ to $20mg$. Samples above the $500\mu g$ in size showed a relatively constant concentration. Smaller samples had a concentration inversely proportional to their weight and were best fit by concentration (% mod) = $2.2 \pm 1.1\mu g$ divided by the sample size in micrograms.

Contamination During Graphitization

The contribution from graphitization can be separated from other sources of contamination by graphitizing small aliquots of the CO_2 obtained from large anthracite samples. The contamination added during graphitization included not only the reaction of the CO_2 with hydrogen over the iron catalyst, but also the transport and the measurement of the CO_2. In Figure 3, the ^{14}C concentration *vs* the inverse mass of the graphitized carbon is shown for nine large sample combustions. Each group of graphitizations was fit to a linear inverse relation to mass, and the average slope (the introduced contamination) was found to be $0.36 \pm 0.19\mu g$. The average intercept of the individual fits was $0.45 \pm 0.20\%$ modern, in good agreement with the $>500\mu g$ data set shown in Figure 2. (Sample C839 was discarded in finding the average intercept because the gas handling system was known to have been badly contaminated with younger organic carbon at the time of its processing.)

The contamination introduced during graphitization was expected to arise predominantly from memory effects of the apparatus. The adsorbed CO_2 or CO on the walls of the apparatus exchanges with the gas in a sample processed later. We attempted to reduce this effect using water vapor as a
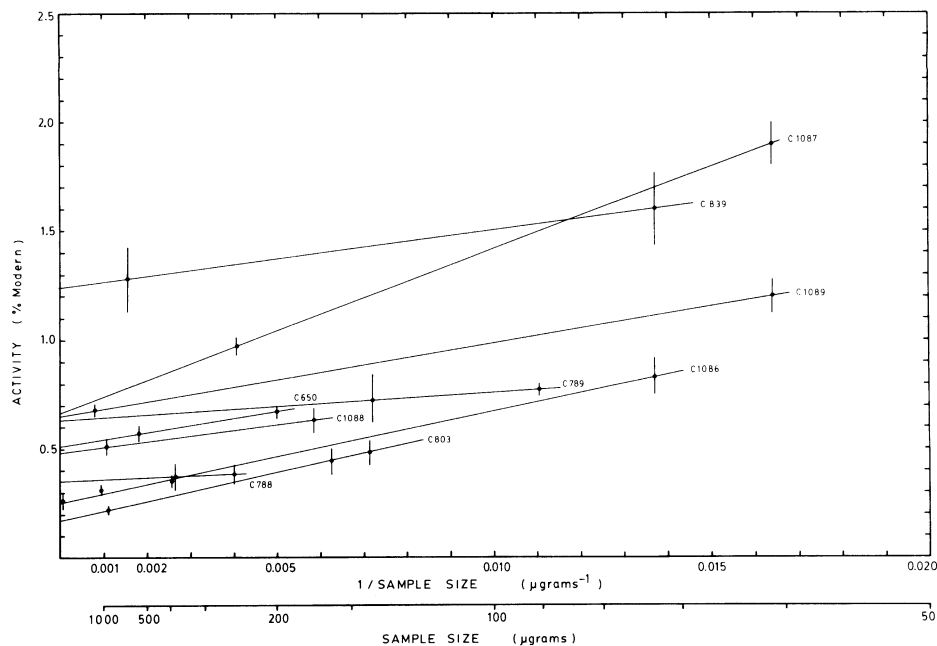
Fig 3. Total system background *vs* the inverse of the graphitized sample size. The anthracite was combusted as large (>1mg) samples and the CO_2 was divided into smaller samples before graphitization.

'cleansing' agent. This was suggested to us by Michael Andrée (pers commun, 1984) and is supported by adsorption theory (de Boer, 1968, p 32). Whenever any part of the apparatus was not in use, it was filled with 20 to 25 Torr of water vapor at ambient temperature. The vapor was evacuated at regular intervals or at the start of the next graphitization. The effect of this procedure was tested by processing anthracite samples directly after processing NBS standard oxalic acid samples, with and without the use of the water vapor cleansing between samples. The cleansing reduced these anthracite backgrounds by factors of 1.5 to 2. The average ^{14}C concentration of all large anthracite samples was reduced from 0.59 ± 0.24% modern to 0.44 ± 0.13% modern by the use of this technique.

We have tried using a number of elements in different forms as graphitizing catalysts. Our usual catalyst was −200 mesh, spherical iron powder of 99% purity. Spherical powders produce the more desirable graphite coating on the catalyst which makes the handling of small samples much easier. One of the likely impurities in the iron, however, would be carbon. Iron placed in the ion source directly from the bottle produced carbon ion beams which were 3 to 4% as intense as beams from graphite-coated iron. These ion beams were long lasting, indicating that the carbon was integral to the iron powder. The ^{14}C concentration of this carbon was found to be 1.5% modern. The initial reduction of the iron before catalysis must remove much of this carbon, or we could not have measured very low ^{14}C

concentrations as we did for the calcite and graphite listed in Table 1. As long as the relative amounts of iron and graphite were similar (within a factor of 2) for all samples, backgrounds, and standards, the contribution of this carbon was small, adding <0.1% modern to the measured ^{14}C concentration of a sample.

Contamination During Storage and Handling

The contamination of the stored graphite by adsorbed gases was checked by comparing the ^{14}C concentration of an anthracite sample which had been stored in a small bottle for 1½ years with the ^{14}C concentration measured when the sample was first produced. Within the uncertainties of the measurements, there was no detectable difference between the earlier and the later measurements. The uncertainties placed an upper limit on this level of contamination of ca 0.2μg modern carbon equivalent.

The contamination of a sample arising from the handling necessary for placing it in the ion source was checked by dividing a processed graphite into a very small sample (ca 50μg) and a large sample (>600μg). The concentrations were measured only after the surface had been sputtered for a few minutes, our usual procedure. The difference between the measured concentrations of the two placed an upper limit on the handling contamination of <0.1μg modern carbon equivalent.

Contamination During Combustion

The measured contaminant levels of the preparation stages discussed so far account for 0.7 ± 0.3μg of the 2.2 ± 1.1μg total system background for very small samples. The remaining 1.5 ± 1.0μg of modern equivalent carbon must come from the only part of the process not discussed so far: the combustion to CO_2.

To test if the copper oxide were the source of the contamination, we tried two approaches. For three very small samples of anthracite, the oxide was substituted with ultra-pure oxygen at 300 Torr. These data are shown in Figure 2, and are indistinguishable from samples combusted with copper oxide. Further, changing the amount of oxide used for combustion by a factor of five did not change the measured ^{14}C concentration of small anthracite samples within the limits of the measurements.

The only remaining component of the combustion procedure was the Vycor tube. As one would expect that the heating of the tubes to 900° C in air prior to loading them would remove any carbonaceous impurities, we had not expected these to cause problems. However, a literature search revealed that Vycor has some alarming properties. It is the most porous of the commercial glasses and is designed to be so (Nordberg, 1944). The effective surface area is 120 to 200m^2 per gram (Emmett & DeWitt, 1943; Schwertz, 1949) with an average pore size of 30 to 60A leading to fractal type surfaces (Dozier, Drake & Klafter, 1986). At dry ice temperatures, 1g of Vycor is capable of adsorbing 50cc of CO_2 at 1atm partial pressure (Emmett & DeWitt, 1943). These properties suggested that the combustion tubes might indeed be the cause of the observed combustion contamination and that we would be wise to use a substitute. However, only Vycor and

quartz can withstand the preferred 900° C combustion temperature, and quartz is second only to Vycor for permeability (Eitel, 1966, p 11). Boutton *et al* (1983) report non-quantitive yields (50–80%) from several organic materials combusted in Pyrex tubes at a lower temperature, but they find almost no isotopic fractionation effects from the low temperature combustion. We tried to combust the anthracite at lower temperatures (550° C) in Pyrex tubes, and did not achieve quantitative yields. However, the total system background using Pyrex tubes for combustion was a factor of two less than that using Vycor: $1.1\mu g$ *vs* $2.2\mu g$ modern carbon, as shown in Figure 2.

CONCLUSION

Table 2 summarizes the identifiable sources of contamination along with the contributions of each to the total system background. Contamination levels are shown as micrograms of modern equivalent carbon added to the sample. Clearly, the most serious contribution was from combustion. Memory effects in the graphitization and the ^{14}C in the iron catalyst were lesser problems. Storage, handling, and ion source cross talk were much less serious.

From these data, we could determine the sample size required to obtain a desired final measurement uncertainty with the present system. The final or total measurement uncertainty was calculated as the quadratic combination of the background uncertainty shown in Figure 2 and the sam-
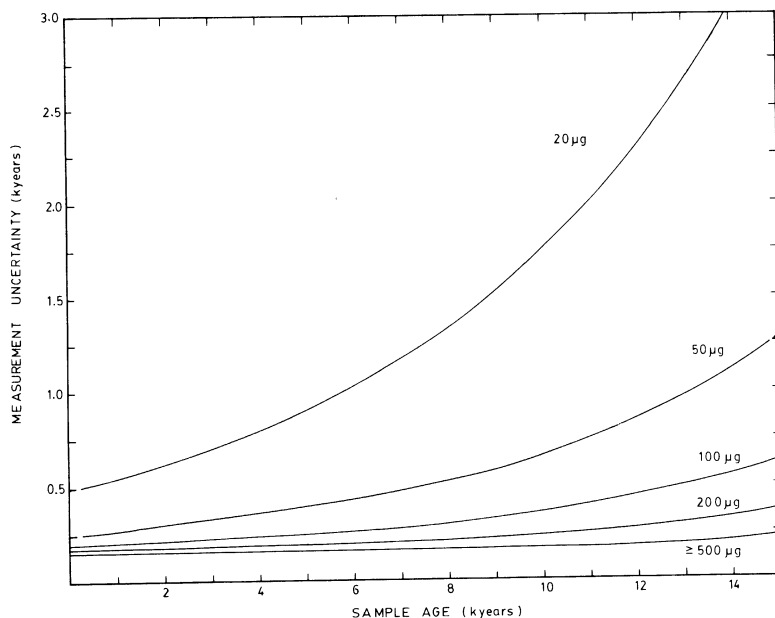

Fig 4. The total measurement uncertainty *vs* Holocene material age for different sample sizes with an assumed measurement precision of 2%. The background was assumed to have the form shown in Fig 2.

ple measurement precision. The sample measurement precision is calculated by our analysis system to be the larger of the two possibilities: the precision found from the counting statistics of the sample and the associated standard measurements, or the standard deviation of the several measurements carried out on that sample. As shown in Figure 4, 200μg of carbon were sufficient for the measurement of Holocene materials to a final uncertainty of 200 years, assuming a 2% (±160 yr) precision in the measurement. For most of the Holocene, 100 and even 50μg carbon samples yield useful age determinations when the sample is limited to these amounts. As an example, the smallest unknown sample that we have dated was a charcoal smudge on a rock that produced only 32μg of carbon. The measured age was 11,000 ± 1200 yr BP, in good agreement with larger bone and charcoal samples from the site.

Figure 5 indicates the final age ranges that would be assigned to late Pleistocene materials having different sample sizes using our present sys-
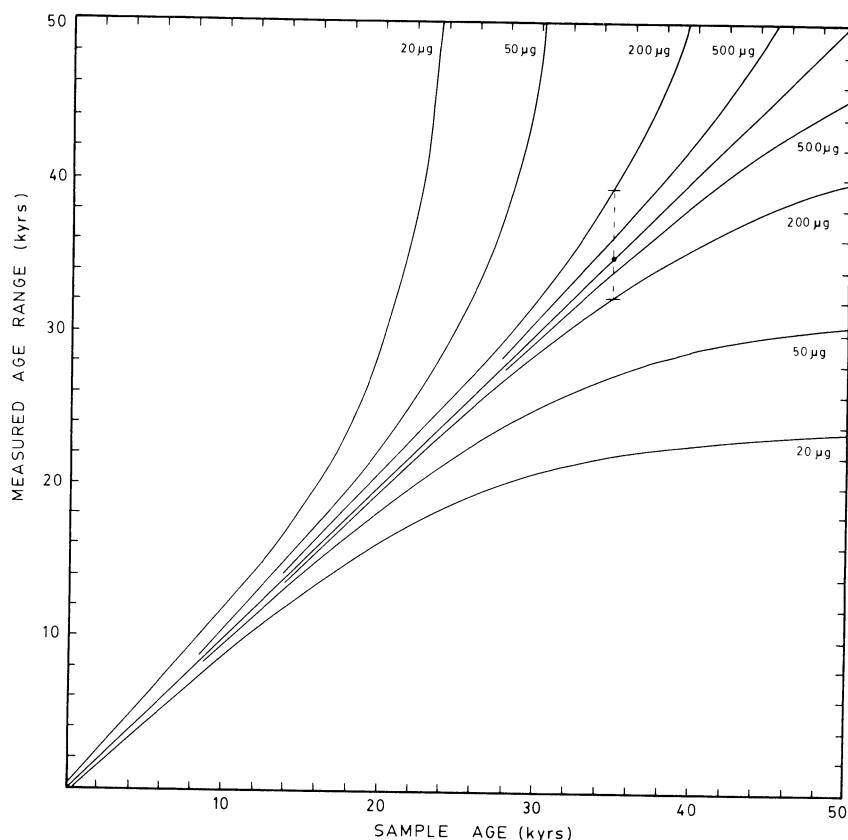

Fig 5. The final measured age range for samples of various sizes assuming a concentration measurement precision of 3% with the background shown in Figure 2. The background uncertainty dominates throughout the late Pleistocene portion of the plot. For example, 200μg of 35 kyr carbon would yield an age range of 32.5 to 39.5 kyr.

tem. A measurement precision of 3% and the background levels from Figure 2 were assumed for all cases. Again, the uncertainty in the background dominates the final uncertainty of the measurement for very small and very old samples. The 20 to $50\mu g$ samples could yield only a limit on the age of Pleistocene materials, but a $500\mu g$ sample is clearly sufficient for age determinations through 40,000 years. For many applications, $200\mu g$ was enough.

Small sample ^{14}C dating using accelerators is already measuring sample sizes considerably smaller than the optimistic projections of ten years ago. With the identification of the sources of much of our total system contamination, we hope to make $100\mu g$ an easily dated sample size throughout much of the range of accelerator ^{14}C dating.

REFERENCES

Boutton, T W, Wong, W W , Hachey, D L, Lee, L S, Cabrera, M P and Klein, P D, 1983, Comparison of quartz and Pyrex tubes for combustion of organic samples for stable carbon isotope analysis: Anal Chem, v 55, p 1832–1833.
de Boer, J H, 1968, The dynamical character of adsorption: Oxford, Clarendon Press.
Dozier, W D, Drake, J M and Klafter, J M, 1986, Self-diffusion of a molecule in porous Vycor glass: Phys Rev Letters, v 56, no. 2, p 197–200.
Eitel, W, 1966, Silicate science, vol 4: New York, Academic Press.
Emmett, P H and DeWitt, T W, 1943, The low temperature adsorption of nitrogen, oxygen, argon, hydrogen, n-butane, and carbon dioxide on porous glass and on partially hydrated chabazite: Jour Am Ceramic Soc, v 65, no. 7, p 1253–1262.
Nelson, D E and Hobson, K A, Simon Fraser University radiocarbon dates I: Radiocarbon, v 24, no. 3, p 344–351.
Nelson, D E, Southon, J R, Vogel, J S, Korteling, R and Ku, T-L, 1984, Progress in 14-C and 10-Be dating at SFU: Nuclear Instruments & Methods, v B5, p 136–143.
Nelson, D E, Vogel, J S, Southon, J R and Brown, T A, 1986, Accelerator radiocarbon dating at SFU, *in* Stuiver, M and Kra, R S, eds, Internatl ^{14}C conf, 12th, Proc: Radiocarbon, v 28, no. 2A, p 215–222.
Nordberg, M E, 1944, Properties of some Vycor brand glasses: Jour Am Ceramic Soc, v 27, no. 10, p 299–305.
Schwertz, F A, 1949, Fluid flow study of porous glass: Jour Am Ceramic Soc, v 32, no. 12, p 390–393.
Vogel, J S, Southon, J R, Nelson, D E and Brown, T A, 1984, Performance of catalytically condensed carbon for use in accelerator mass spectrometry: Nuclear Instruments & Methods, v B5, p 289–293.