

HIGH-SENSITIVITY RADIOCARBON DATING IN THE 50,000 TO 70,000 BP RANGE WITHOUT ISOTOPIC ENRICHMENT

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ABSTRACT. Calculations show the possibility of detecting ^{14}C remaining after 10 or 11 decay half-lives in natural materials, such as wood, using commercially available liquid scintillation (LS) detectors. Assuming *in-situ* ^{14}C production has contributed insignificantly to the measured ^{14}C , one can calculate finite ages approaching 70 ka. In practice, defensible finite age determinations involve careful considerations of several critical elements in the procedure. These critical elements are: 1) the integrity of the sample itself, in terms of younger contaminants and of *in situ*-produced ^{14}C ; 2) the availability of "dead" background material; 3) chemical blank in laboratory preparation of, in this case, benzene; and 4) stability of background and efficiency of the LS counting system. High-sensitivity ^{14}C dating reveals a low level of memory effect ^{14}C in benzene synthesized in the laboratory from anthracite or marble. This level of ^{14}C activity is equivalent to that found in 53 ka old wood, and thus, is not distinguishable from petrochemical benzene used in routine dating. If careful control of laboratory conditions can maintain this ^{14}C blank constant, reproducible dating beyond 53 ka would be possible. Although we have not completed a systematic analysis of the origins of memory effect, lithium reactors used in acetylene production and organic solvents in wood pretreatment are likely sources.

INTRODUCTION

The specific activity of modern (pre-industrial) ^{14}C after 11 half-lives ($11 \times 5730 = 63,030$ yr) of decay is 0.00662 disintegrations per minute (dpm) per gram of carbon. By convention (Stuiver & Polach 1977), a sample must have a count rate $>2\sigma$ above background, to have a finite age assigned to it. To measure such low levels of ^{14}C activity, a ^{14}C dating system must have a low and steady background to minimize the statistical uncertainty in the background, and the sample under examination must have as much carbon as is practical to minimize the statistical uncertainty in the sample count rate. Unfortunately, counter backgrounds and sample size are positively correlated (Stuiver, Robinson & Yang 1979). Longer counting times improve the statistical resolution of low-count-rate samples, but the longer the counting time, the greater the probability of electronic shifts in background or efficiency. Approaches to this problem include: 1) development of special counters with extremely high active volumes and/or very low backgrounds (Oeschger & Wahlen 1975; Povinec 1992); 2) the use of isotopic enrichment to concentrate the ^{14}C into normal volume gas proportional counters; and 3) the use of large volume (>10 g of carbon), high-stability, low-background liquid scintillation counting (LSC) systems. The high density of carbon and low cosmic-ray profile in a vial of benzene potentially give a high sample-to-background count-rate ratio. Recent developments in LSC technology take advantage of these attributes of benzene for high-sensitivity ^{14}C dating.

The only finite ^{14}C dates in the 60–70 ka range now available were obtained by CO_2 gas proportional counting after isotopic enrichment by thermal diffusion (Grootes *et al.* 1975; Grootes 1977, 1978; Grootes *et al.* 1980). This method works well and has produced numerous finite range dates up to about 75 ka BP. Its disadvantages are that it requires over 100 g of carbon and the use of an elaborate *ca.* 4-m-tall column and bulb apparatus for 45 days. LSC also has the potential of detecting low levels of ^{14}C (Gupta & Polach 1985; Polach 1987). The purpose of this study is to

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investigate the detection limits of ^{14}C (high-sensitivity ^{14}C dating) in real samples using the latest LSC measurement technology, and to evaluate different chemical phases for minimizing contamination with younger carbon. Here we report on our recent investigations into the ^{14}C detection limits of the entire LSC system, including all chemical and physical steps in the process. To illustrate, we tested a wood specimen from Alaska, whose expected age was 125 ka BP. Our radiometric analysis yielded ^{14}C at the 50 ka level. Whether this is the correct age, an artifact of the chemical pretreatment procedure, or of *in-situ* production is uncertain.

METHODS

The LSC technique employed in this study requires the laboratory synthesis of benzene, with all six benzene carbon atoms derived from the sample. See Noakes *et al.* (1963) for details of the basic benzene synthesis procedure. Wood and anthracite coal samples were processed in this study; samples were combusted to CO_2 , which then reacted with hot lithium to form Li_2C_2 . Addition of tritium-free water to the cooled lithium carbide produced acetylene; then the acetylene was catalytically ($\text{Cr}_2\text{O}_5/\text{Al}_2\text{O}_3$) trimerized to benzene. A scintillant compound (butyl-PBD) was dissolved in the benzene, and the benzene counted for 12 k min. Each benzene sample in the present study contained 11.5 g of carbon. Routine counting in this laboratory employs up to 2.6 g of carbon counted for 2 k min.

In addition to increasing the sample size and counting time for this study, it was necessary to consider all suspected contributors to ^{14}C in the sample which were not radioactive decay remnants of the original ^{14}C incorporated in the growing tree. Possible sources of extraneous ^{14}C are: 1) environmental carbon while wood was *in situ*; 2) carbon in sample pretreatment reagents; and 3) carbon in benzene synthesis reagents and apparatus (system memory effects). Sources 2 and 3 are often called chemical blanks. In addition, all β -counting systems have a counter background, which is the minimum count rate of a sample containing no ^{14}C . Only 1 part of modern carbon contaminant per 2000 parts of "infinitely old" carbon will produce an apparent ^{14}C age of 63 ka. Therefore, both counter background and chemical blank must be minimized, and their values and variabilities must be well known and statistically well behaved. Kalin and Long (1989) previously discussed counter background; we discuss below the measures taken in this study to minimize environmental contamination and chemical blank for dating old wood.

In this study, a white spruce wood (*Picea glauca*) sample, collected in 1987, was provided by Dr. Troy Péwé of Arizona State University. The sample (Péwé No. 187) was taken from the Eva Creek Forest Bed at its type locality, 16 km west of Fairbanks, Alaska. Figure 1 shows the geological section from which the specimen was taken. We chose this sample as a geological blank because it is believed to have grown during the last interglacial, *ca.* 125 ka ago (Péwé 1975, written communication 1991; Westgate 1988). This wood specimen is well preserved, because it was overlain by 15 m of permafrost soil until recent mining trenching. The specimen was not rooted in place.

Laboratory processing included first an inspection to identify portions with no visible degeneration, and then sampling only the firmest and freshest-appearing portions. For cellulose preparation, 300 g of selected wood were ground to sawdust size for extraction of waxes and resins by ultrasound, with a mixture of 67% toluene and 33% ethanol. The wood was then ultrasonically washed again in ethanol, and then extracted in a Soxhlet apparatus with ethanol. LSC of the toluene indicated no counts in the ^{14}C spectrum. The scintillation spectrum from the ethanol indicated that it derived from fermentation of modern plants. After Soxhlet extraction, the sample was oven dried, and the remaining solvent was removed by boiling in water and oven drying. The boiling step was designed to remove possible extraneous mobile sugars and laboratory solvents used in pretreatment,

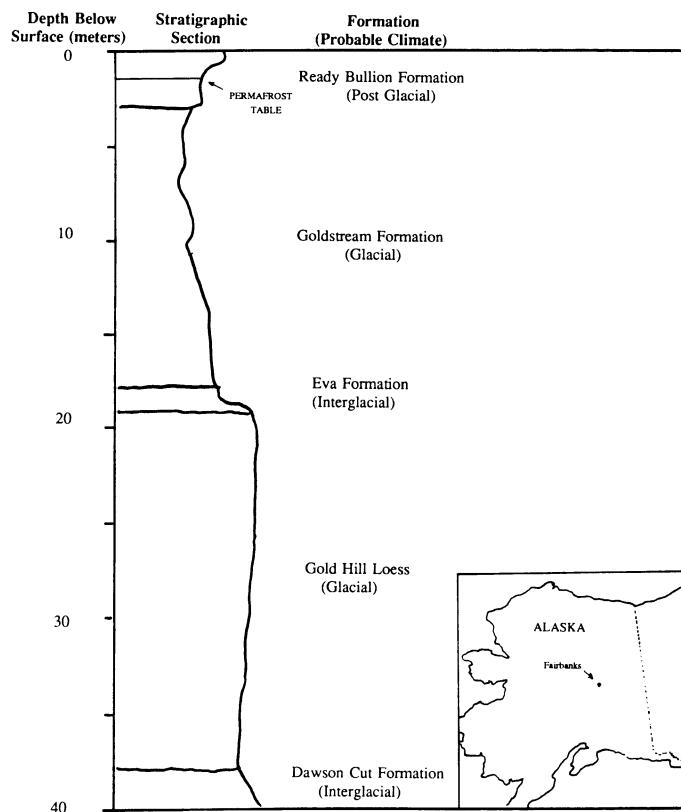


Fig. 1. Stratigraphic section from the Eva Creek locality (redrawn from Péwé (1975))

such as alcohol, which are more volatile than water. The bleaching step involved sodium hypochlorite solution acidified with phosphoric acid, and heated to 90°C until the wood was light tan (first of two runs) or paper white (second run), indicating removal of lignin.

In the combustion procedure, oxygen was passed through a Vycor glass tube containing a sample heated by gas-burner flames. Standard purity tank-gas oxygen may contain traces of atmospheric CO₂ (Grootes *et al.* 1975). We passed the oxygen through a tube filled with Ascarite™ to remove CO₂ before entering the combustion tube. The carbon collected in our Ascarite filter was measured at about 36 pMC. To minimize memory effects from previous samples, the entire system is thoroughly cleaned between samples. This is routine and effective in normal processing, but insufficient for high-sensitivity ¹⁴C dating. As we illustrate below, it is necessary to dedicate combustion-lithium-catalysis lines to high-sensitivity dating, and to purge these lines by combusting ¹⁴C-free samples before processing samples to be dated.

After combustion, the CO₂ is reacted with lithium at about 600°C to form Li₂C₂. Any contaminant carbon in the lithium will also react to Li₂C₂ at this time. Each purchase of lithium is from a batch selected for highest purity and lowest carbon content. Exposure to air during loading of the lithium reactor, though minimized as much as possible, inevitably exposes lithium pellet surfaces to atmospheric CO₂, possibly adding to the sample blank. Our records show, however, no difference in sample blank, for routine samples, between the first lithium from a freshly-opened can to the last lithium in the can. In these high-sensitivity tests, we used the same fresh batch of lithium for all samples. Previous experiments (Radnell & Muller 1980) demonstrated that the stainless steel lithium reactor can be a source of ¹⁴C memory effects. Routine mechanical and chemical cleaning

cannot eliminate all memory of previous high-activity samples. It is assumed that carburization and decarburization of steel, possibly in micropores in the reactor inner surface, is responsible for this effect (Radnell & Muller 1980).

The next step is the hydrolysis of lithium carbide with pure, tritium-free water to produce acetylene. The acetylene is then trimerized to benzene by adsorption onto a catalyst of Cr_2O_5 on Al_2O_3 pellets starting at 25°C, but this exothermic reaction can raise the reaction temperature to about 50°C. We used the identical catalyst for the series of anthracite purges and for the test sample.

The two independent determinations of the Eva Creek sample were separated by several months, and each was preceded by two (first run) or four (second run) anthracite samples processed through the same lines, using the same catalysts. Anthracite is considered to have undetectable levels of ^{14}C . The purpose of the anthracite runs was to purge the lines and catalysts of any ^{14}C memory of the previous standard runs. Each sample run produced over 12 g of benzene. All samples, anthracites, wood specimens and modern standards were counted for 12 k min in a Quantulus (LKB-Wallac) LS detector; the detector is located in a temperature- and humidity-controlled underground counting room, with 10 m of concrete and soil overburden. The Quantulus stores the energy spectra of the cumulative counts, and allows energy discrimination. Count rates were recorded every 50 min for statistical analysis. See Kalin and Long (1989) for more complete description of the counting system.

RESULTS

The Quantulus LS counters are set to minimize the effect of spectral shifts on ^{14}C detection efficiency (described in McCormac 1992). The present configuration detects 71.723% of the ^{14}C disintegrations in the benzene. Table 1 shows standard and background count rates (and $\delta^{13}\text{C}$ data)

TABLE 1. Standard and Background Count Rates for 12 g Benzene

Sample	Counts per minute $\pm 1 \sigma$	$\delta^{13}\text{C} (\text{\textperthousand}) \pm 1 \sigma$
<i>Long and Kalin (1992) (old data - Quantulus no. 3)</i>		
Spec. benzene	0.9244 \pm 0.0088	-30.5 \pm 0.2
Calib 83.2 (Anthracite)	Not counted	
Calib 83.3 (Anthracite)	1.0375 \pm 0.0093	-23.4 \pm 0.2
A-5883 (Wood)	1.0919 \pm 0.0095	-21.1 \pm 0.2
Calib 98 (ANU sucrose)	157.2153 \pm 0.1145	-10.2 \pm 0.2
<i>Long and Kalin (this study - Quantulus no. 4)</i>		
Spec. benzene	1.2334 \pm 0.0101	-30.5 \pm 0.2
Calib 83.8 (Anthracite)	1.5496 \pm 0.0227	-23.8 \pm 0.2
Calib 83.6A (Anthracite)	1.2772 \pm 0.0206	-24.0 \pm 0.2
Calib 83.6B (Anthracite)	1.2544 \pm 0.0204	-24.0 \pm 0.2
Calib 83.7 (Anthracite)	1.2614 \pm 0.0103	-23.8 \pm 0.2
A-5883.3 (Wood)	1.4214 \pm 0.0109	-20.5 \pm 0.2
Calib 114	173.770 \pm 0.1204	-10.6 \pm 0.2

for 12 g of benzene. The different values for background between the first and second runs reflect the two different Quantulus counters used for the two experiments. Figure 2 histograms illustrate the effect of run sequence in the same vacuum lines on the chemical blank. A sequence of anthracite samples showed a decreasing level of memory effect. Complete removal of memory effect requires two runs of anthracite. Figure 2A represents the first run on Péwé Sample 187, Figure 2B, the second. Figure 2C shows the memory effect resulting from a 10 × modern sample, followed by anthracites. The "zero" level in all three figures is the background set by spectrophotometric benzene (Table 1).

Ages for samples run at routine precision in this laboratory are calculated using spectrophotometric benzene as the background. With 3 ml of benzene counted for 2 k min, differences in ¹⁴C activity between spectrophotometric benzene and anthracite are statistically invisible. In the high-sensitivity mode, it is necessary to subtract the ¹⁴C activity of the chemical blank from the sample count rate to correctly determine the ¹⁴C activity of the wood sample. The best chemical blank would be a wood specimen known to be too old to contain measurable ¹⁴C, and which has been subjected to the same chemical and physical processing as the wood specimen of age to be determined. At the onset of this series of experiments, the white spruce specimen (Pewé no. 187) was thought to be such a chemical blank. Here we assume, until further experiments indicate otherwise, that this specimen represents our chemical blank. Thus, in high-sensitivity ¹⁴C dating by LSC, we evidently have three levels of background/blank, listed in order of increasing ¹⁴C activity: 1) spectroscopic benzene (not processed in laboratory); 2) anthracite-derived benzene (pretreated with inorganic solvents, then processed through laboratory); and 3) >100 ka cellulose (pretreated with organic solvent, then processed through laboratory).

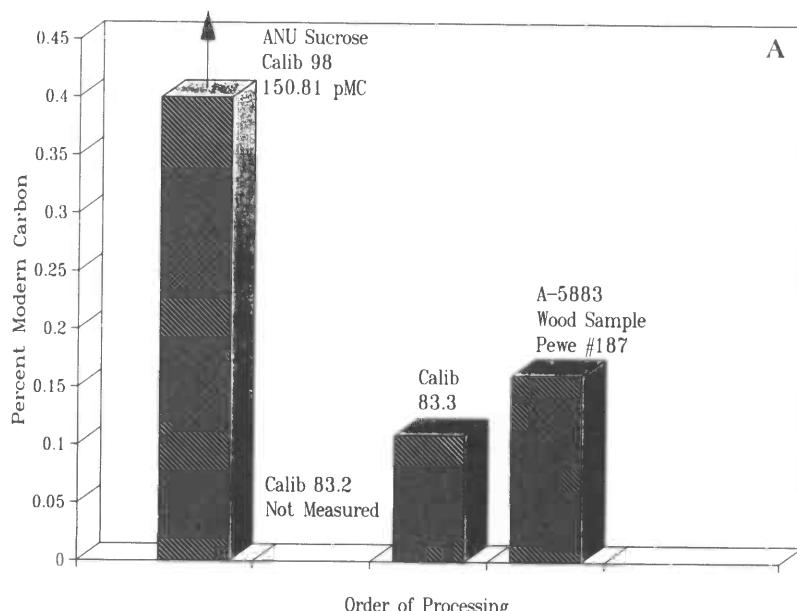


Fig. 2. Histograms showing count rates of a series of standard, then anthracite samples preceding the two runs of the Eva Creek Spruce wood sample and a test with a sample containing enriched ¹⁴C. A. Memory effect of ANU sucrose in the combustion/benzene synthesis system for the 1990 series of runs.

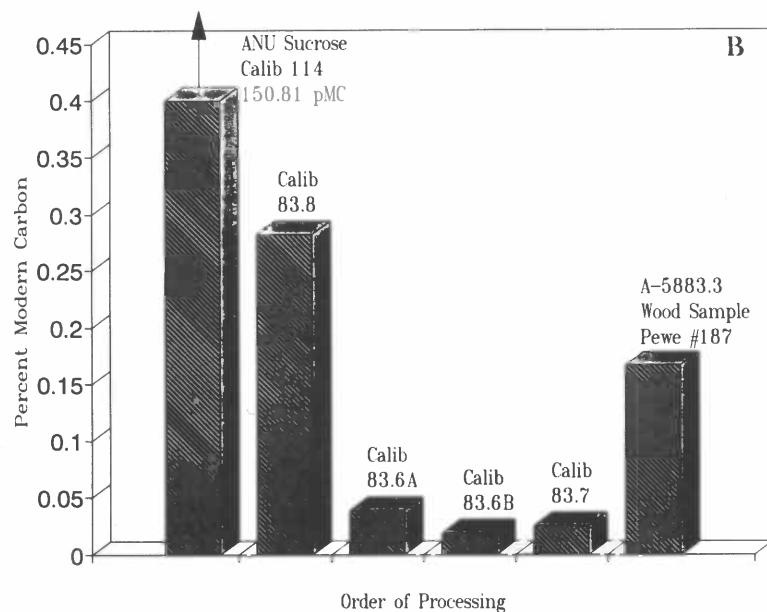


Fig. 2B. Memory effect of ANU sucrose in the combustion/benzene synthesis system for the 1992 series of runs.

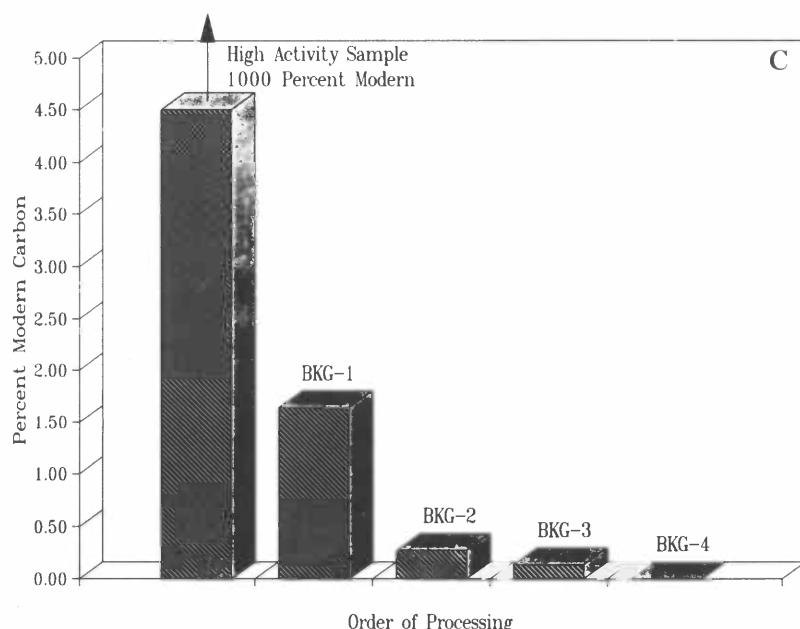


Fig. 2C. Memory effect resulting from a 10 x modern sample (ANU isopropyl alcohol) followed by anthracite runs in the combustion/benzene synthesis system. Note scale difference.

DISCUSSION

The best estimate of the age of the wood specimen, based on its species and sedimentary position at time of collection, is 125 ka BP. The fact that the calculated ¹⁴C age for this wood specimen strongly disagrees with the stratigraphic age requires re-examination of the arguments leading to both age conclusions. Here, we focus only on the ¹⁴C age obtained in this study. *In-situ* production of ¹⁴C is considered highly unlikely to produce an apparent age this young (A. J. T. Jull, personal communication 1992).

Based on spectrophotometric benzene as the background, the calculated ages of the wood specimen from near Fairbanks, Alaska are 51,640 +790/-710 BP (first run, 1990, reported in Long & Kalin 1992) and 51,230 +790/-710 BP (second run, 1991, this study). Note that the two calculated ages are statistically indistinguishable. These dates show the reproducibility of high-sensitivity ¹⁴C analyses in two different Quantulus counters separated by almost a year, but they cannot represent the age of the wood specimen, because spectrophotometric benzene is not a chemical blank at this level of sensitivity. Figure 2B suggests that one anthracite following a sample of modern ¹⁴C activity is insufficient to purge all remnants of ¹⁴C from the system. A similar experiment, following ANU isopropyl alcohol with 10 × modern ¹⁴C activity run through the entire vacuum system (Fig. 2C) demonstrated that two purges are needed. This experiment further implies that reaction with surfaces of the lithium reaction vessel contributes significantly to the chemical blank.

Based on the average of the 3rd and 4th anthracites in Figure 2B as the chemical blank, the age calculated for Péwé no. 187 is 52,530 +780/-710 BP. The calculated age actually published in Long and Kalin (1992) was 60,330 +3120/-2230 BP. This differs from the 52,530 BP date, because the 60,330 BP result is based on an erroneously high value for the anthracite chemical blank. If calculated based on the average of the 3rd and 4th anthracite blanks in Figure 2B, the ¹⁴C levels in the two analyses of the wood sample are statistically identical.

The remaining choice for chemical blank is the wood specimen, itself. If this turns out to be the correct blank, then the process of cellulose extraction contributes to the ¹⁴C activity of the final benzene produced at the 52 ka level, reproduced in two experiments separated by a year. The answer to the question of solvent-introduced ¹⁴C blank awaits ¹⁴C analysis of a 2 Ma wood specimen, pretreated without organic solvents, now in process in our laboratory.

The calculated age based on spectrophotometric benzene as background is equivalent to 0.1862 pMC. Thus, a wood sample with 0.1862% contamination with modern carbon would have an apparent ¹⁴C age of 51,420 BP (based on the conventional 5568-yr half-life). Table 2 summarizes the possible sources of contaminant and the measures taken in this study to eliminate them.

Thus, the ¹⁴C blank above the levels found in anthracite can be separated into 2 components: 1) chemical pretreatment – either non-removable substances from the soil, or remnants of solvents from laboratory processing; and 2) combustion/synthesis system. In these experiments, the chemical treatment component is the larger – ca. 15 mg of modern carbon equivalent in the wood sample. The combustion/synthesis system contributed only slightly more than 2 mg modern carbon equivalent.

Assuming that chemical pretreatment contamination is a solvable problem, either by elimination or by compensation, and that the variance of the chemical blank is comparable to that of counting statistics, the maximum determinable finite age, using this system and the 2 σ criterion, is 69 ka conventional ¹⁴C yr (71 ka, based on the 5730-yr half-life).

TABLE 2. Possible Sources of Contamination in Wood Specimen

Contaminant source in wood specimen	Laboratory procedure for minimization	Estimated contribution to chemical blank
Carbonate carbon in sediments	Acid treatment	None
Organic carbon in sediments	Extract cellulose fraction for dating	Unmeasurable; cellulose rare in alluvial sediments
Microbiological growth in wood	Selected most solid segments for processing	Microscopic examination yields no evidence.
Reagents in chemical treatment procedure	Only alcohol contains ^{14}C ; sample boiled in water to remove alcohol	Possible, but unlikely; ethanol not used in anthracite preparation. Estimate 0.005 cpm
Combustion apparatus and chemicals in acetylene prep.	Present in all samples; anthracite compensates	
Apparatus and catalyst in benzene preparation	Present in all samples; anthracite compensates	Unknown
Memory effect in counting vials	Thoroughly wash and dry <i>in vacuo</i>	Unmeasurable
Scintillant cocktail	Present in all samples, including spec. benzene	Estimate 0.006 cpm

SUMMARY, CONCLUSIONS AND FUTURE WORK

Measurement of ^{14}C in natural materials has always required considerable care and attention to minute sources of contamination. Over the course of the maturation of the technique, the detection limit, in terms of maximum finite ages obtainable, has improved, from *ca.* 20 ka with the original elemental carbon counters (Arnold & Libby 1951; Anderson, Arnold & Libby 1951), to gas proportional counters at *ca.* 55 ka (Stuiver, Robinson & Yang 1979), to isotopic enrichment – gas proportional counting (Grootes 1975) at *ca.* 75 ka. The present experiments suggest that if the inorganic pretreatment chemical blank is shown to be reproducible within counting statistics, LSC is capable of extended range ^{14}C dating to *ca.* 70 ka. Regardless of the ^{14}C detection technique employed, old samples are particularly susceptible to contaminant ^{14}C from the natural, precollection environment. Other sources of contamination are technique-dependent. The LSC process requires several more steps than gas proportional counting, but it does not require isotopic enrichment. With extreme care, the LSC technique should be able to extend the dating range to within one half-life of the current maximum limit of ^{14}C dating set by isotopic enrichment.

Tests are underway on more wood samples from Alaska and Canada, which are clearly associated with deposits even older than the one in this study. These samples have been pretreated without using organic solvents, and thus, will help resolve the question of ^{14}C blank.

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