

ROBUST RADIOCARBON DATING OF WOOD SAMPLES BY HIGH-SENSITIVITY LIQUID SCINTILLATION SPECTROSCOPY IN THE 50–70 KYR AGE RANGE

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ABSTRACT. Although high-sensitivity liquid scintillation (LS) spectroscopy is theoretically capable of producing finite radiocarbon ages in the 50,000- to 70,000-yr range, there is little evidence in the literature that meaningful dates in this time period have been obtained. The pressing need to undertake calibration beyond 26 kyr has resulted in the regular publication of ^{14}C results in excess of 50 kyr, yet very little effort has been made to demonstrate their accuracy or precision. There is a paucity of systematic studies of the techniques required to produce reliable dates close to background and the methods needed to assess contamination from either in situ sources or laboratory handling and processing. We have studied the requirements for producing accurate and reliable dates beyond 50 kyr. Laboratory procedures include optimization of LS spectrometers to obtain low and stable non- ^{14}C background count rates, use of low-background counting vials, large benzene volumes, long counting times, and preconditioning of vacuum lines. We also discuss the need for multiple analyses of a suitable material containing no original ^{14}C (background blank) and the application of an appropriate statistical model to compensate for variability in background contamination beyond counting statistics. Accurate and reproducible finite ages >60 kyr are indeed possible by high-sensitivity LS spectroscopy, but require corroborating background blank data to be defensible.

INTRODUCTION

Possible sources of contamination limiting the maximum determinable radiocarbon age, T_{\max} , (Gupta and Polach 1985) have previously been examined and identified independently by Long and Kalin (1992) and McCormac et al. (1993), using large benzene volumes in modern liquid scintillation (LS) systems. Both stated that a T_{\max} (defined by the 2- σ above-background convention described by Stuiver and Polach [1977]) of about 70 kyr was theoretically possible, but acknowledged that reliable dates beyond 50 kyr are rarely obtained.

Long and Kalin (1992) investigated the detection limits for wood samples in modern LS equipment. They reduced the ^{14}C activity of their vacuum lines by successive anthracite blanks before analyzing 125-kyr subfossil wood pretreated to holocellulose. Non- ^{14}C background arising from other activities in the counting vials, photomultiplier tubes, and spectrometer materials, as well as from cosmic rays that eluded the anti-coincidence shield, was defined using spectrophotometric benzene, which was assumed to be ^{14}C “dead.” They obtained ^{14}C ages for the wood of about 51 kyr (0.18 pMC), and postulated that significant contamination was derived from the holocellulose extraction process, and specifically, the use of ethanol as a solvent.

McCormac et al. (1993) also studied the factors that influence the background level and its variability and concluded that the lithium used for the generation of acetylene was the principal source of ^{14}C contamination. As evidence, they advanced the observation that resynthesized spectrophotometric benzene produced a higher counting rate than its parent material, and further, that it was similar to the rate from 125-kyr subfossil wood. This suggested that ^{14}C was added during combustion and benzene synthesis rather than pretreatment. It was shown, moreover, that vacuum line contamination

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levels could be lowered by processing several ^{14}C -dead samples prior to synthesis of old samples. Both studies unfortunately stopped short of the multiple ^{14}C -dead blank analyses required to investigate these issues more thoroughly.

The present work re-examines the factors limiting the maximum determinable age for ^{14}C dating by high-sensitivity LS spectroscopy. It presents the results of 19 measurements on ancient wood independently dated beyond 100 kyr, and 12 measurements on spectrophotometric benzene, and uses these data to evaluate the variability in the apparent ^{14}C ages of the wood blanks after pretreatment and benzene synthesis. Armed with this information, high-sensitivity ^{14}C measurements of 12 sequential 100-yr blocks of wood from an ~60-kyr subfossil log were analyzed in 2 different ways to compensate for ^{14}C background and its variability. The 2 approaches are compared, and a transparent statistical approach for determining standard errors for older samples is introduced.

EXPERIMENTAL PROCEDURES

Use of Ancient Wood as a Chemical Blank

Long and Kalin (1992) list the availability of ^{14}C -dead background material as one of the critical elements in the quest for obtaining reliable dates near the limits of the ^{14}C method. Clearly, ancient wood in excess of 100 kyr is the ideal chemical blank for studies investigating ancient subfossil wood.

Hogg (2004) introduced the ~110-kyr Airedale Reef Ancient Wood standard (here described as ARAW-I) obtained from a coastal section in North Taranaki, New Zealand. In addition to this, 2 new standards have been obtained for this study:

1. A second Airedale Reef standard (ARAW-II) composed of totara (*Podocarpus totara*) logs obtained from an intertidal marine platform stratigraphically below the ARAW-I standard and dated by associated volcanic deposits to about 125 kyr (Newnham and Alloway 2001).
2. Kauri (*Agathis australis*) logs contained within an oxygen isotope stage (OIS) 7 (>140 kyr, Marra *et al.* 2006) intertidal platform in Manukau Harbor near Auckland airport, New Zealand.

These ancient wood blank standards in this study were subjected to exactly the same pretreatment processes and benzene synthesis procedures as the unknown-age samples.

Pretreatment Procedures

Long and Kalin (1992) cite pretreatment processes (in particular the use of organic solvents) as a potential source of laboratory contamination for the dating of samples close to background in age. They isolated the holocellulose fraction with solvent extraction (toluene and ethanol, then water) followed by 2 successive bleaches with sodium hypochlorite solution acidified with phosphoric acid. The residue after the second bleach was white in color, and they used this property as an indication of complete lignin removal.

Hoper *et al.* (1998) recommended removal of all lignin to ensure that the fraction isolated for dating is as representative as possible of prevailing atmospheric conditions at the time of growth. They extracted holocellulose using solvent extraction (ethanol/chloroform, ethanol, and water) followed by bleaching with sodium chlorite acidified with hydrochloric acid, but they added a further alkali extraction to produce a pure α -cellulose component.

Hua *et al.* (1999) catalogued various pretreatment procedures used in studies measuring ^{14}C in modern tree rings. The most common pretreatment method was acid-alkali-acid extraction (AAA, also

referred to as acid-base-acid [ABA]). Some researchers added an additional solvent extraction step to the AAA process, while others isolated the holocellulose component by the additional use of sodium chlorite/hydrochloric acid. The authors state that the AAA process does not remove all of the mobile materials through which wood can become contaminated by modern contaminants. Clearly, there is no universally accepted procedure for wood pretreatment, and Hua et al. (1999) consider this to be a major contributing factor to the discrepancies in the modern ¹⁴C data sets.

Hogg (2004) also utilized the α -cellulose fraction of wood for determining blank background levels used in routine dating. He modified the solvent extraction procedure described by Hopet et al. (1998), substituting acetone derived from a petrochemical source for the ethanol-chloroform and ethanol solvents. This avoids the use of ethanol, which has modern levels of ¹⁴C if derived from the fermentation of plants.

The same α -cellulose extraction procedure as that described in Hogg (2004) is used in this study.

Optimization of the LS Spectroscopy Method

Polach et al. (1984) introduced the “total optimization” concept in which all known parameters affecting accuracy and reproducibility are fully optimized to obtain the best results. To achieve this, it is necessary to optimize spectrometer performance, vial type, benzene volume, analysis time, and to precondition vacuum lines.

Spectrometer Optimization

PerkinElmer Wallac Quantulus spectrometers were used in this study. The instrument has extensive passive shielding (650 kg), which is thickest at the zenith where background-forming cosmic rays are concentrated. It also has an active guard composed of a plastic scintillator that is operated in anti-coincidence with the photomultiplier tubes in order to further reduce cosmic-ray background. In addition, electronic circuitry reduces cross-talk between the opposed photomultiplier tubes. These measures combine to result in an instrument that has unsurpassed low and stable background count rates (Polach et al. 1988).

Vial Type

Neither Long and Kalin (1992) nor McCormac et al. (1993) specify vial design or composition, but it can be assumed from earlier publications (Pearson 1979; Kalin and Long 1989) that 20-mL, carefully screened, low-potassium glass counting vials were used in their studies. Hogg et al. (1991) and Hogg and Noakes (1992) concluded that for spectrometers using true anti-coincidence detection and extensive passive shielding (as in the Quantulus), synthetic silica or Teflon® vials produced the highest signal to noise ratio. They also noted that synthetic silica had superior physical properties to Teflon, the physical properties of which have caused counting difficulties for some researchers (e.g. Devine and Haas 1987; Kalin and Long 1989). Hogg (1993) described the Waikato 10-mL synthetic silica counting vial with excellent counting characteristics and physical properties designed for high-sensitivity counting applications. The design is based upon the standard 20-mL LS counting vial and consists of a flat-bottomed synthetic silica cylindrical cell, 50-mm high and 28-mm in outer diameter, with a stainless steel and brass stopper. The seal is provided by a Greene, Tweed black chemraz O-ring that is expanded onto the inside walls of the silica cell by the multicomponent metal stopper. The entire stopper assembly is shielded from the photomultiplier tubes by an opaque Delrin cap.

Benzene Volume

Hogg (1993) showed that maximum determinable age increases with sample benzene weight. This relationship was investigated further for this study by determining T_{\max} for a variety of synthetic silica vials with varying benzene volumes and a counting time of 3000 min (Figure 1). There is a rapidly decreasing benefit beyond 7.5 g benzene because of the logarithmic nature of the curve. The added resolution gained by using larger amounts of benzene (as in the Kalin and Long [1992] and McCormac *et al.* [1993], 12 g and 13.13 g benzene, respectively) is disproportionate to the extra effort and resources required to generate the larger volumes. For this reason, we have used 7.5 g of benzene in this study.

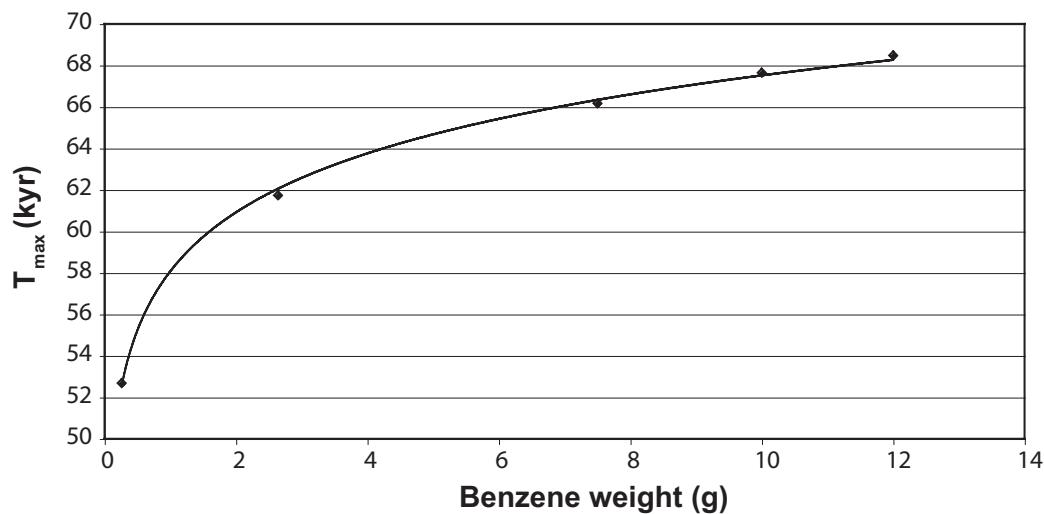


Figure 1 Maximum determinable age (T_{\max}) plotted against benzene weight counted in synthetic silica counting vials of varying volumes. T_{\max} for the 5 benzene weights shown was calculated from background and modern count rates measured in 3 Waikato silica vial sizes (0.3 g benzene in 0.5-mL minivials; 2.6 g benzene in 3-mL standard vials; 7.5 g, 10 g, and 12 g benzene in 10-mL vials).

Count Time

McCormac *et al.* (1993) and Long and Kalin (1992) utilized counting times of 13k min and 12k min per sample, respectively. These studies, however, involved relatively small numbers of samples. A plot showing the influence of counting time on the magnitude of standard errors due to counting statistics alone for a ~60-kyr sample using 7.5 g benzene in 10-mL Waikato vials is given in Figure 2 (solid line). In practice, there is an additional source of uncertainty over and above counting statistics due to sample-to-sample variability in contamination. This is quantified in a subsequent section using the 19 measurements on the ancient wood blanks, where it is shown that in the present case it adds an additional uncertainty of 0.017 pMC to each measurement. The dashed line in Figure 2 shows the magnitude of the error term after inclusion of this additional uncertainty. One important implication of this research is that ultimate precision is equally dependent upon the variability in contamination levels as on counting times and that there is very little to be gained by extending counting times beyond about 10k min per sample (see further discussion below).

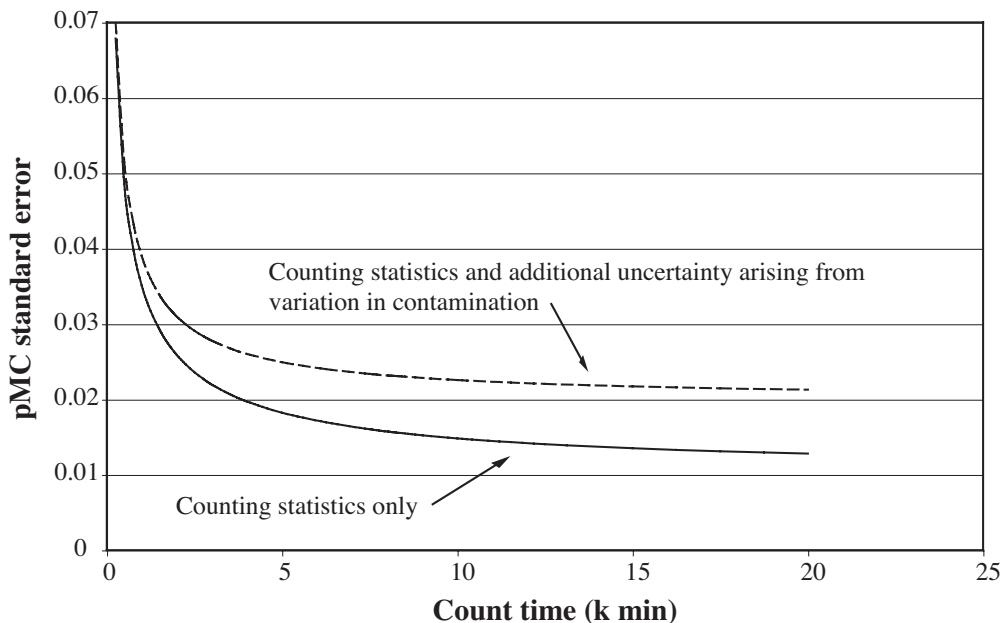


Figure 2 Standard error plotted against count time for a ~60-kyr wood sample using 7.5 g benzene in Waikato 10-mL vials. The solid line represents counting statistics alone. The dashed line includes an additional uncertainty of 0.017 pMC that accounts for the variability in contamination (see text for further details). Data based upon University of Waikato measurements.

Preconditioning of Vacuum Lines

McCormac et al. (1993) and Long and Kalin (1992) clearly showed that vacuum line contamination levels are significantly reduced by initially processing 2 ¹⁴C-dead samples. We followed this procedure by starting each batch of old samples by processing a minimum of 2 ancient wood standards.

NON-¹⁴C BACKGROUND CALIBRATION OF LS VIALS

In LS counting, there is an unavoidable count rate that arises not from ¹⁴C decay, but from other sources. Sources include α -, β -, and γ -ray activities in the vial material, photomultiplier tubes, other components of the spectrometer or the room, as well as cosmic rays that elude the passive and active shields. These various radiations may enter the benzene and interact there, producing scintillation events that may be indistinguishable from a ¹⁴C decay. This “non-¹⁴C background” may be quantified by filling the vials with fossil fuel-derived benzene, which is assumed to contain no ¹⁴C. Note that the non-¹⁴C background can, and does, vary from vial to vial since the materials of the vials themselves contribute to the counting rate. Six vials were used in the study, and the non-¹⁴C background was determined for each vial individually.

Of course, this procedure is not valid if the fossil fuel-derived benzene itself contains activities (including, but not limited to, ¹⁴C) that are not present in the benzene synthesized from real samples. In order to investigate this possibility, 3 brands of benzene were analyzed:

1. Sigma-Aldrich Chromasolv® Plus for high-performance liquid chromatography (HPLC);
2. Scharlau benzene for liquid scintillation;
3. Ajax Chemicals analytical reagent (AR) grade.

Although all 3 benzene types gave comparable count rates, the Ajax AR benzene pulse-height spectrum was significantly different in shape from either benzene synthesized in the Waikato laboratory or the higher grade Sigma-Aldrich Chromasolv Plus and Scharlau LS benzenes (see Figure 3 for ^{14}C pulse-height spectra). We are unsure if this is due to a dissolved chemical quench or possible contamination by ^3H , but recommend that only spectrograde benzene be used for non- ^{14}C background calibration.

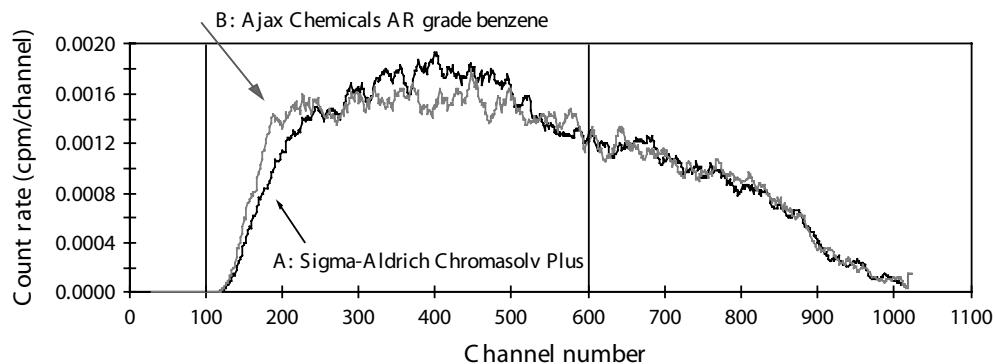


Figure 3 ^{14}C pulse-height spectra for A) Sigma-Aldrich benzene Chromasolv® Plus for high-performance liquid chromatography (HPLC) and B) Ajax Chemicals analytical reagent (AR) grade benzene. There is a significant difference in spectral shape, particularly in the 100–300 channel range. The vertical lines represent the lower (channel 100) and upper (channel 600) discriminator levels used to define the ^{14}C window throughout this study.

In the course of the present work, 6 different vials were used. At least 2 and up to 4 measurements of spectrophotometric benzene were performed for each vial. Each measurement employed 7.5000 ± 0.0002 g of benzene, and counting times were 10k min per measurement. Typical non- ^{14}C background counting rates within the ^{14}C window on the pulse-height spectrum (see Figure 3) were 0.6 counts per minute (cpm).

^{14}C RESULTS FOR ANCIENT WOOD BLANKS

A total of 19 samples of the ancient wood blanks were pretreated to α -cellulose. Benzene was then synthesized in vacuum lines that had been preconditioned by first passing at least 2 ancient wood samples through them. Table 1 shows the measured counting rate for each of these samples (column 3), together with the average non- ^{14}C background (column 4) for the specific vial in which each was measured (column 2). Column 5 is the difference between these two, which is interpreted as the contribution from any ^{14}C in the sample. This ^{14}C signal may be converted to a percentage of Modern Carbon (pMC) using measurements on oxalic II standards run in the same vials. The results are shown in Table 1 (column 6) and in Figure 4. The first 17 blanks shown in Table 1 (ARAW-I and -II) are derived from *P. totara* logs, with the remaining 2 (18 and 19) derived from *A. australis* wood. There does not appear to be any inter-specific variation. The 19 measurements span a range from 0.030 to 0.115 pMC and have a mean value of 0.070 pMC.

A chi-squared (χ^2) test indicates that the variability in this data set is not accounted for by counting statistics alone. Define normalized χ^2 as

$$\chi^2/\nu = 1/(n-1) \times \sum_i (pMC - 0.070)^2 / \sigma_i^2$$

Table 1 Ancient wood (AW) blank count rates, weight-normalized to 7.5 g benzene, before and after subtraction of the non-¹⁴C background (as determined with spectrobenzene in each vial). The net count rate for the ancient wood samples is converted to pMC using count rates (see Table 2) for OX-II modern standards in each individual vial.

Lab identifier	Vial #	AW cpm	Spectrobenzene cpm	Net AW cpm	Net AW pMC
14693S-1 ^a	3	0.674 ± 0.008	0.622 ± 0.004	0.052 ± 0.009	0.065 ± 0.011
14694S-1 ^a	1	0.670 ± 0.008	0.619 ± 0.005	0.051 ± 0.009	0.064 ± 0.011
14695S-1 ^a	2	0.680 ± 0.008	0.625 ± 0.006	0.054 ± 0.010	0.068 ± 0.012
14696S-1 ^a	3	0.681 ± 0.008	0.622 ± 0.004	0.059 ± 0.009	0.074 ± 0.012
14698S-1 ^a	1	0.712 ± 0.008	0.619 ± 0.005	0.093 ± 0.010	0.115 ± 0.012
14699S-1 ^a	2	0.667 ± 0.007	0.625 ± 0.006	0.042 ± 0.009	0.053 ± 0.011
14700S-1 ^a	3	0.660 ± 0.008	0.622 ± 0.004	0.039 ± 0.009	0.048 ± 0.011
14701S-1 ^a	6	0.689 ± 0.008	0.621 ± 0.005	0.068 ± 0.010	0.085 ± 0.012
14701S-2 ^a	4	0.704 ± 0.008	0.641 ± 0.005	0.063 ± 0.010	0.078 ± 0.012
14701S-3 ^a	6	0.665 ± 0.008	0.621 ± 0.005	0.044 ± 0.010	0.055 ± 0.012
14701S-4 ^a	9	0.719 ± 0.009	0.637 ± 0.006	0.082 ± 0.010	0.101 ± 0.013
14843S-1 ^b	2	0.649 ± 0.008	0.625 ± 0.006	0.024 ± 0.010	0.030 ± 0.012
14843S-2 ^b	9	0.703 ± 0.008	0.637 ± 0.006	0.066 ± 0.011	0.082 ± 0.014
14843S-3 ^b	4	0.689 ± 0.008	0.641 ± 0.005	0.048 ± 0.012	0.059 ± 0.014
14843S-4 ^b	9	0.696 ± 0.008	0.637 ± 0.006	0.059 ± 0.012	0.074 ± 0.014
14843S-5 ^b	4	0.717 ± 0.009	0.641 ± 0.005	0.076 ± 0.012	0.094 ± 0.015
14843S-7 ^b	1	0.697 ± 0.008	0.619 ± 0.005	0.078 ± 0.009	0.097 ± 0.011
17031S-1 ^c	3	0.670 ± 0.008	0.622 ± 0.004	0.048 ± 0.009	0.060 ± 0.011
17031S-2 ^c	2	0.668 ± 0.007	0.625 ± 0.006	0.043 ± 0.009	0.053 ± 0.012
<i>Weighted average</i>				0.070 ± 0.003	
<i>Galbraith mean</i>				0.071 ± 0.005	

^aAncient wood type: Airedale Reef totara I (ARAW-I).

^bAncient wood type: Airedale Reef totara II (ARAW-II).

^cAncient wood type: Manukau kauri.

where σ_i is the statistical uncertainty on pMC_i , and n ($= 19$) is the number of measurements. Then, χ^2/v for this data set of 19 measurements is 3.0, whereas the maximum value for an acceptable fit at the 5% level is only 1.6 (i.e. there is only a 5% probability that χ^2/v is greater than 1.6). Hence, it is necessary to add an additional random uncertainty to each data point to take into account the additional variability resulting from sample-to-sample variations in contamination. Galbraith (2005: 100) gives a rigorous statistical prescription for doing this and for calculating the resulting mean and its associated uncertainty. A summary of this method is given in the Appendix. The result is included in Table 1 and indicates that the mean contamination in these ancient wood blanks is 0.071 pMC, equivalent to an apparent age of 58,200 ¹⁴C yr. The additional uncertainty that must be added in quadrature to the statistical uncertainty for each sample to account for the sample-to-sample variability in the contamination is 0.017 pMC, which is closely similar to the counting statistics for our specific case of 10k min counting times and 7.5 g of benzene. This is an important result because it implies that there is a finite level of precision obtainable in ¹⁴C dating and that this level may be more closely related to the variability in contamination levels than to analysis times. It strengthens the conclusion that for this study there is little to be gained from counting the samples for more than 10k min.

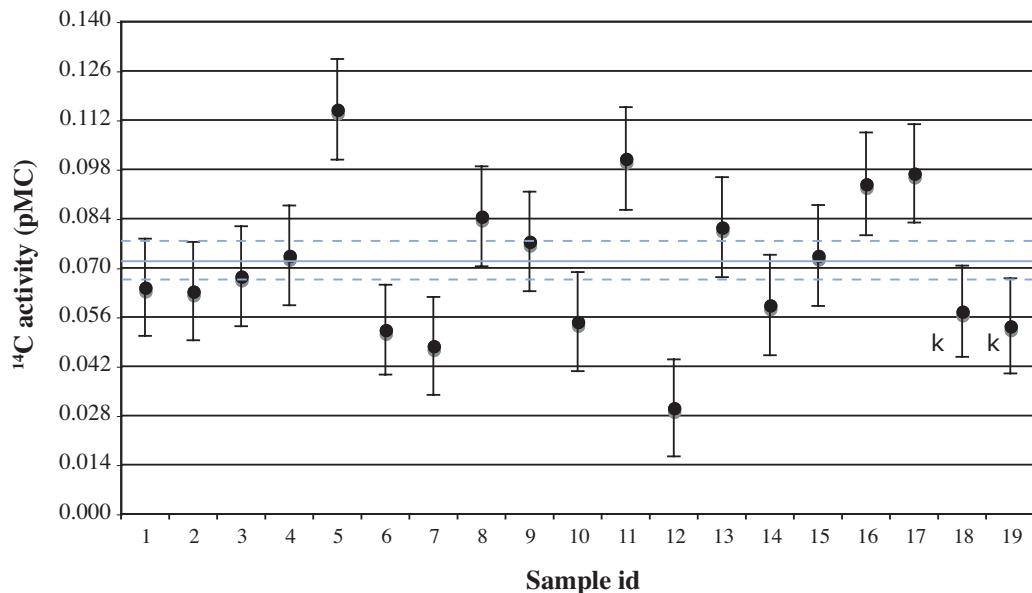


Figure 4 ¹⁴C activity for ancient wood blanks counted in Waikato 10-mL synthetic silica vials. Counting time = about 10k min per sample; benzene weight = 7.5 g. Samples prefixed with the letter "k" identify Manukau kauri blanks. Gray solid and dotted lines represent Galbraith mean ± 1 standard deviation (see Table 1 for details).

ANALYSIS OF "UNKNOWN" SAMPLES

The analyses on the ancient wood blanks provide a measure of both the level and the variability of any contaminating ¹⁴C, either not removed by sample pretreatment or added during α -cellulose extraction or benzene synthesis. For any other sample processed in the same way, it is necessary to subtract the contribution from this contamination in order to determine its intrinsic ¹⁴C activity. There are 2 possible approaches. The traditional approach, used by Long and Kalin (1992), is to subtract the mean ¹⁴C activity of the ancient wood from the measured ¹⁴C activity of the sample. Here, we introduce a second, alternative approach for compensating for contamination that eliminates the need for spectrobenzene measurements by directly subtracting the ancient wood count rates from the count rate of the "unknown" sample. The 2 methods are outlined below.

Method 1: Removal of the Contamination Contribution by Subtraction of the Mean ¹⁴C Activity of the Ancient Wood

In this traditional approach, the ¹⁴C activity of the ancient wood is determined as described above. Similarly, the ¹⁴C activity of the "unknown" sample is determined from the measured count rate by subtracting the non-¹⁴C count rate (derived from the spectrobenzene) and converting the difference to an activity. But this activity is the sum of intrinsic ¹⁴C and the ¹⁴C due to contamination. The latter is therefore removed by subtracting the ¹⁴C activity of the ancient wood. This process is illustrated in Table 2 for the subfossil tree discussed below.

This approach has the advantage of using a large number of ancient wood blanks to determine the average contamination because it is vial-independent. It has the disadvantage of requiring multiple measurements of spectrobenzene for each vial.

Table 2 ¹⁴C results for 12 consecutive 100-ring blocks extracted from a subfossil kauri log containing 1200 rings (Duder/Bibby tree 4441) using Method 1 for removing the contribution from contamination. The non-¹⁴C background is defined using spectrobenzene (column 3). The net count rate is converted to activity (pMC - column 6) using the vial-specific count rate of the modern standard (column 5). The contribution from contamination, taken as the Galbraith mean activity of the 19 ancient wood samples (0.071 ± 0.005 pMC from Table 1), can then be subtracted (column 7). Only 3 vials (numbers 1, 2, and 3) were used in the analysis of the 12 unknown samples.

Wk-no. 15-	Sample gross cpm	Spectro- benzene cpm	Sample net cpm	Mod Std cpm ^a	Sample pMC	Sample pMC contamination subtracted
590	0.724 ± 0.011	0.619 ± 0.005	0.105 ± 0.012	79.770 ± 0.097	0.131 ± 0.014	0.060 ± 0.015
591	0.718 ± 0.011	0.622 ± 0.004	0.096 ± 0.012	79.916 ± 0.097	0.120 ± 0.015	0.049 ± 0.015
592	0.727 ± 0.011	0.625 ± 0.006	0.101 ± 0.012	79.824 ± 0.097	0.126 ± 0.015	0.055 ± 0.016
670	0.717 ± 0.008	0.622 ± 0.004	0.095 ± 0.009	79.916 ± 0.097	0.119 ± 0.011	0.048 ± 0.012
671	0.728 ± 0.009	0.619 ± 0.005	0.109 ± 0.010	79.770 ± 0.097	0.136 ± 0.012	0.065 ± 0.013
672	0.707 ± 0.009	0.625 ± 0.006	0.082 ± 0.010	79.824 ± 0.097	0.102 ± 0.013	0.031 ± 0.014
673	0.713 ± 0.009	0.622 ± 0.004	0.091 ± 0.010	79.916 ± 0.097	0.113 ± 0.012	0.042 ± 0.013
674	0.733 ± 0.009	0.625 ± 0.006	0.107 ± 0.010	79.824 ± 0.097	0.133 ± 0.013	0.063 ± 0.014
730	0.729 ± 0.008	0.619 ± 0.005	0.110 ± 0.009	79.770 ± 0.097	0.137 ± 0.011	0.066 ± 0.013
731	0.720 ± 0.011	0.622 ± 0.004	0.098 ± 0.012	79.916 ± 0.097	0.122 ± 0.015	0.051 ± 0.016
732	0.722 ± 0.010	0.619 ± 0.005	0.103 ± 0.011	79.770 ± 0.097	0.128 ± 0.014	0.057 ± 0.015
733	0.735 ± 0.011	0.625 ± 0.006	0.109 ± 0.012	79.824 ± 0.097	0.136 ± 0.015	0.065 ± 0.016

^aCount rate from an OX-II standard normalized to 100 pMC and $\delta^{13}\text{C} = -25\text{\textperthousand}$.

Method 2: Removal of the Contamination Contribution by Directly Subtracting the Raw Count Rates for the Ancient Woods on a Vial-by-Vial Basis

This approach does not require that the non-¹⁴C background of individual vials be determined with spectrobenzene. Rather, it utilizes the ancient wood samples directly for determining the combination of non-¹⁴C background and contamination for each individual vial. Table 3 shows the count rates for the ancient wood blanks sorted by vial number. A weighted average count rate, called the “AW background” in Table 3, is calculated for each vial by the Galbraith model as outlined above. This method suffers because of the relatively small number (2–4) of ancient wood background determinations per vial, making any extreme values more influential. Four of the 6 vials (numbers 2, 3, 4, and 9) show variability within counting statistics; the remaining 2 vials (1 and 6) have more variable ancient wood backgrounds, and this is reflected in the larger average vial background errors computed by the Galbraith model.

Table 4 illustrates this second method for the subfossil tree that is discussed further below.

¹⁴C RESULTS FOR A WOOD SAMPLE CLOSE TO BACKGROUND IN AGE

The ancient wood blank analyses permit the computation of contamination level and variability. To determine how best to apply these data, we measured ¹⁴C concentration in 12 consecutive 100-ring blocks extracted from a subfossil kauri log containing 1200 rings (Duder/Bibby tree 4441), near the limit of the ¹⁴C dating method. The results of the 12 measurements are given in Tables 2 and 4 and shown graphically in Figure 5. $\delta^{13}\text{C}$ values cluster tightly and range from -21.5 to $-22.0\text{\textperthousand}$.

The data shown in Figure 5 span 1100 calendar yr, since the mid-points of the 100-yr blocks range from ring 50 to ring 1150. Although there is no obvious trend in the pMC as a function of ring num-

Table 3 Count rates for ancient wood (AW) blanks, normalized to a weight of 7.5000 g and sorted by vial number.

Vial #	Lab identifier	Norm cpm	Norm cpm error
1	14694S-1	0.670	0.008
1	14698S-1	0.712	0.008
1	14843S-7	0.697	0.008
<i>Average vial 1 AW background</i>		0.693	0.010
2	14695S-1	0.680	0.008
2	14699S-1	0.667	0.007
2	14843S-1	0.649	0.008
2	17031S-2	0.668	0.007
<i>Average vial 2 AW background</i>		0.666	0.005
3	14693S-1	0.674	0.008
3	14696S-1	0.681	0.008
3	14700S-1	0.660	0.008
3	17031S-1	0.670	0.008
<i>Average vial 3 AW background</i>		0.671	0.004
4	14701S-2	0.704	0.008
4	14843S-3	0.689	0.008
4	14843S-5	0.717	0.009
<i>Average vial 4 AW background</i>		0.703	0.006
6	14701S-1	0.689	0.008
6	14701S-3	0.665	0.008
<i>Average vial 6 AW background</i>		0.677	0.009
9	14701S-4	0.719	0.009
9	14843S-2	0.703	0.008
9	14843S-4	0.696	0.008
<i>Average vial 9 AW background</i>		0.706	0.005

ber, a linear least-squares fit yields a change in ^{14}C age of 1400 yr over this interval. The uncertainty is large, however, with the $1-\sigma$ range encompassing ^{14}C intervals from -800 to 3300 yr.

Method 1 results in a weighted average of 0.054 ± 0.004 pMC, with the 12 measurements passing a χ^2 test: $\text{df} = 11$ $\chi^2/v = 0.63$ (5% 1.8). Method 2 results are very similar (average = 0.059 ± 0.004 pMC) and again pass a χ^2 test: $\text{df} = 11$ $\chi^2/v = 1.2$ (5% 1.8). These ^{14}C concentration data convert to ^{14}C ages of $60,400 \pm 630$ and $59,800 \pm 590$ yr, respectively. Both methods for compensating for contamination appear to give similar results with little to distinguish them.

CONCLUSIONS

High-sensitivity LS spectroscopy is indeed capable of achieving finite ^{14}C ages >60 kyr. This can only be accomplished by use of high-performance and low-background LS spectrometers such as the PerkinElmer Quantulus, low-activity counting vials with good physical properties such as the Waikato 10-mL silica vials, high benzene weights of at least 7.5 g, long counting times of 10k min per sample, and preconditioned vacuum lines.

Table 4 ¹⁴C results for 12 consecutive 100-ring blocks extracted from a subfossil kauri log containing 1200 rings (Duder/Bibby tree 4441) using Method 2 for removing the contribution from contamination. Tree-ring numbers are given in column 1. This method uses the average count rates for the ancient woods (column 5) to define the combined contributions from non-¹⁴C background and contamination for each individual vial. The differences between these and the gross cpm from the samples may then be converted directly to contamination-corrected activity (pMC) values (column 8).

Tree-ring #	Wk-no. 15-	Vial #	Ancient wood		Mod Std cpm	Sample pMC	
			Sample gross cpm	background cpm ^a			
1–100	590	1	0.725 ± 0.011	0.693 ± 0.010	0.032 ± 0.015	79.770 ± 0.097	0.039 ± 0.018
101–200	591	3	0.718 ± 0.011	0.671 ± 0.004	0.047 ± 0.012	79.916 ± 0.097	0.058 ± 0.015
201–300	592	2	0.727 ± 0.011	0.666 ± 0.005	0.061 ± 0.012	79.824 ± 0.097	0.075 ± 0.015
301–400	670	3	0.717 ± 0.008	0.671 ± 0.004	0.046 ± 0.009	79.916 ± 0.097	0.057 ± 0.011
401–500	671	1	0.729 ± 0.009	0.693 ± 0.010	0.036 ± 0.013	79.770 ± 0.097	0.044 ± 0.016
501–600	672	2	0.707 ± 0.009	0.666 ± 0.005	0.041 ± 0.010	79.824 ± 0.097	0.051 ± 0.013
601–700	673	3	0.713 ± 0.009	0.671 ± 0.004	0.041 ± 0.010	79.916 ± 0.097	0.052 ± 0.012
701–800	674	2	0.733 ± 0.009	0.666 ± 0.005	0.067 ± 0.010	79.824 ± 0.097	0.083 ± 0.013
801–900	730	1	0.729 ± 0.008	0.693 ± 0.010	0.037 ± 0.013	79.770 ± 0.097	0.046 ± 0.016
901–1000	731	3	0.720 ± 0.011	0.671 ± 0.004	0.049 ± 0.012	79.916 ± 0.097	0.061 ± 0.015
1001–1100	732	1	0.722 ± 0.010	0.693 ± 0.010	0.029 ± 0.014	79.770 ± 0.097	0.036 ± 0.018
1101–1200	733	2	0.735 ± 0.011	0.666 ± 0.005	0.069 ± 0.012	79.824 ± 0.097	0.085 ± 0.015

^aData from Table 3.

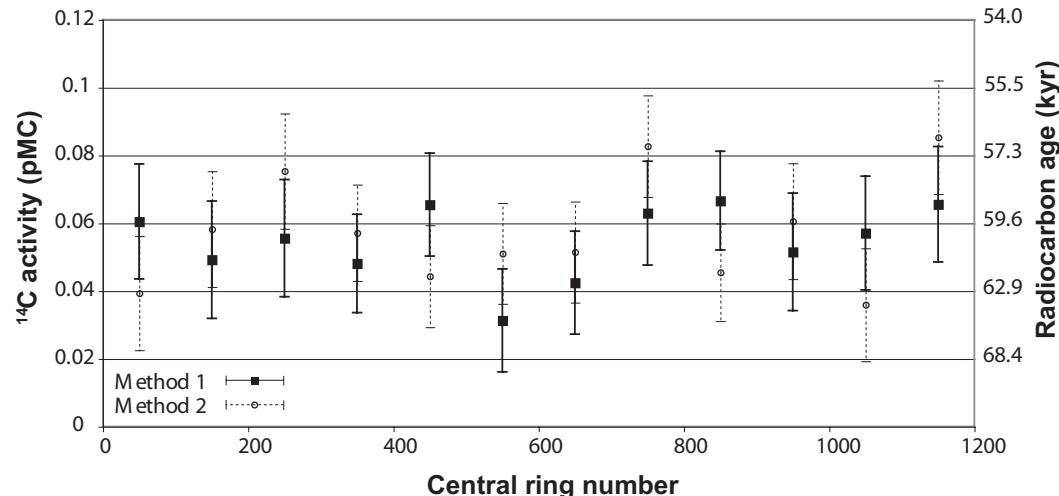


Figure 5 ¹⁴C activities and ages for 12 consecutive 100-ring blocks extracted from a subfossil kauri log (Duder/Bibby tree 4441). Method 1 uses the traditional approach where an average blank activity is calculated and subtracted from the sample activity. Method 2 utilizes the ancient wood blanks directly for calibrating the vial backgrounds (see text for more details).

Meaningful dates in this age range can only be obtained if sample contamination in situ by more recent carbon is removed as far as possible and contamination during handling and processing in the laboratory is minimized.

The degree of success in eliminating in situ contamination depends upon the efficacy of the pretreatment method, which should be α -cellulose extraction if old wood samples are being dated. Multiple analyses of a suitable background blank to assess the degree of residual contamination, and its variability, can allow accurate compensation for the contribution from contamination.

Contamination can be compensated for in 2 ways. The first utilizes multiple measurements of spectrobenzene to define the non- ^{14}C background and subtracts this from both the ancient wood blanks and the unknown-age samples. The second uses the ancient wood blanks directly to define the combined background due to non- ^{14}C sources and ^{14}C contamination. Each method has its advantages and drawbacks. In the present work, we found no statistically significant difference between the 2 prescriptions.

If blank activity measurements show variability beyond counting statistics, an additional random uncertainty should be added to sample results to compensate for this. A technique developed by Galbraith (2005) has been used in this study.

The additional random uncertainty resulting from variability in contamination levels may ultimately define maximum determinable ages, limiting the usefulness of extended counting.

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APPENDIX

The Galbraith Method for Incorporating Variability in the Blank Over and Above Counting Statistics (from Hogg et al. 2006)

Adopting the notation of Galbraith, assume that each individual measurement on an ancient wood blank, $z_u \pm \sigma_u$, is drawn from a Normal population with mean β_u and standard deviation σ_u . If there is an additional source of variability over and above the counting statistics (in this case due to sample-to-sample variation in the removal of contamination), then β_u is randomly drawn from a Normal population with mean μ and standard deviation σ . Together, these imply that z_u is drawn from a Normal population with mean μ and standard deviation $\sqrt{\sigma^2 + \sigma_u^2}$, i.e. σ is an additional uncertainty to be added in quadrature to each measurement to account for the additional variability.

It can be shown that the maximum likelihood estimates of μ and σ satisfy the equations

$$\mu = \frac{\sum_{u=1}^n w_u z_u}{\sum_{u=1}^n w_u} \quad (1)$$

and

$$\sum_{u=1}^n w_u^2 (z_u - \mu)^2 = \sum_{u=1}^n w_u \quad (2)$$

where $w_u = 1/(\sigma^2 + \sigma_u^2)$.

Equations (1) and (2) can be solved numerically to obtain best estimates of μ and σ , denoted by $\hat{\mu}$ and $\hat{\sigma}$. These estimates have approximate standard errors given by

$$se(\hat{\mu}) = \left(\sum_{u=1}^n w_u \right)^{-\frac{1}{2}} \quad \text{and} \quad se(\hat{\sigma}) = \left(2\sigma^2 \sum_{u=1}^n w_u^2 \right)^{-\frac{1}{2}}.$$