

RADIOCARBON DATING BEYOND 50,000 YEARS BY LIQUID SCINTILLATION COUNTING

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ABSTRACT. The maximum age that can be determined by ¹⁴C dating using the LSC method is primarily limited by the background count rate. Improved passive and active shielding have greatly reduced background contributions, but the level that remains limits the theoretical maximum determinable age to *ca.* 70 ka. In practice, reliable dates beyond 50 ka are rarely obtained. We studied the factors that influence the background level and its variability, and found that the standard benzene synthesis techniques for LSC result in increased variability of background levels and restricted extension of the technique back in time. Background benzene samples, obtained from synthesized background material (*e.g.*, anthracite) and from back-burned spectrophotometric benzene, always show activity above spectrophotometric benzene levels. We attribute this to the presence of ¹⁴C in the lithium used for the generation of acetylene. The presence of ¹⁴C in the lithium requires that a constant stoichiometry be maintained between lithium and CO₂ (including any excess used in the reaction), or background variability will be increased. Variation in background due to counter instability also limits the range of ¹⁴C dating. We describe a method to optimize the ¹⁴C counting window for maximum stability and the best figure of merit within the limits imposed by balance-point counting.

INTRODUCTION

Very old samples in the 50–70 ka age range have a ¹⁴C disintegration rate (0.032–0.003 dpm g⁻¹) that is low compared to typical instrument background levels, making reliable dating of very old samples difficult. By using large samples and long counting periods (*e.g.*, 15 ml benzene for 10,000 min) a modern liquid scintillation counter with a stable background (1.25 cpm/13.13 g in the Belfast laboratory; 0.92 cpm/12.0 g in the Arizona laboratory) can theoretically date samples as old as 70 ka using the 2 σ above-background-level convention described by Stuiver and Polach (1977). Despite this, reliable dates beyond 50 ka are rarely obtained.

The selection of a suitable background material is a critical prerequisite to the dating of very old samples. Ideally, the background sample, vial and cap should be identical to the material that is to be dated, with the exception that it “should” contain no ¹⁴C. Anthracite and ancient carbonates are commonly used as “dead” carbon sources from which benzene background samples are synthesized. Alternatively, one may use spectrophotometric benzene produced from a petrochemical source. When counted for very long periods, spectrophotometric benzene shows no detectable ¹⁴C disintegrations and yields a lower background count rate than benzene produced from the anthracite or carbonate source. This indicates that ¹⁴C is either present in the background material, added during pretreatment or added during benzene synthesis. Any combination of all three is also possible. To determine if ¹⁴C is added during the combustion and synthesis process, we burned spectrophotometric benzene and collected the CO₂. We reconverted the CO₂ to benzene through our benzene synthesis apparatus, and compared the count rate from the initial sample with that of the reconverted sample. We found that the synthesized spectrophotometric benzene produced a similar count rate to carbonates and 125 ka subfossil wood, indicating that ¹⁴C is added during combustion and synthesis. Anthracite that we measured produced a higher count rate than subfossil wood or back-burned benzene. This may be due to ¹⁴C added during pretreatment or by microbial and fungal activity in the anthracite (Lowe 1989; Vogel, Nelson & Southon 1987).

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Reaction vessel memory effects can also contribute to background variations. Carbon exchange with the lithium furnace vessel wall (Belfast vessels are made from Type 304 stainless steel, which is austenitic; Tucson vessels are made from Inconel) is responsible for a transfer of carbon to successive samples processed through the rigs (Natesan & Kasner 1970). Even when great care is taken to clean the reaction vessel between samples, we still observe a memory effect. Radnell and Muller (1980) showed that this effect can be as large as 1%. However, by converting several "dead" carbon samples prior to our actual background synthesis, we can effectively remove this as a source of background variation.

Instrument stability is also critical to ensure minimal background variability. By careful choice of operating parameters, it is possible to optimize a counter for dating old samples. We describe here a computer method for selecting the counting window width and the lower level discriminator value for optimal stability.

BACK-BURNING BENZENE

To study the effect of combustion and synthesis on the ^{14}C activity of samples, we burned spectrophotometric benzene and reconverted the resultant CO_2 to benzene. With this process, both the original and final samples can be compared directly without any pretreatment processes that might introduce further contamination. Figure 1 shows our experimental apparatus for back-burning

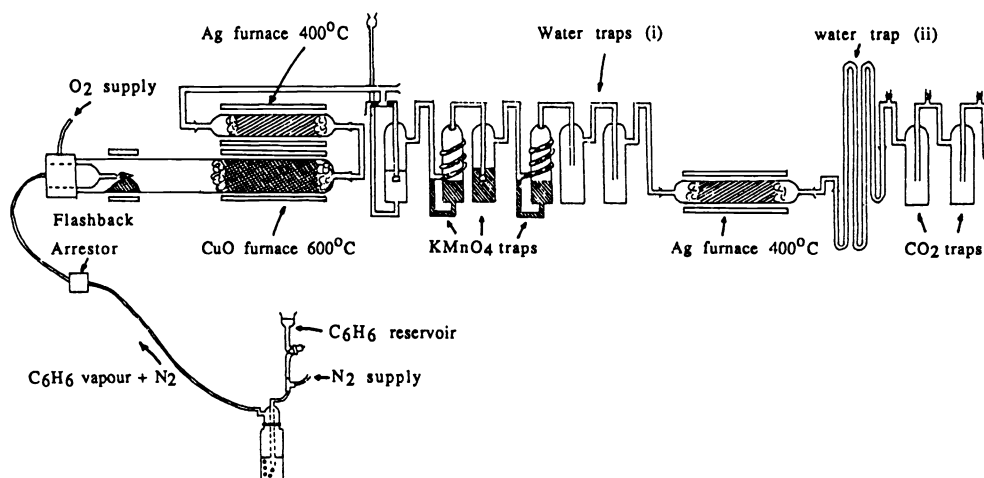


Fig. 1. Experimental apparatus for burning back spectrophotometric benzene. See text for operation.

spectrophotometric benzene. Nitrogen is bubbled through the benzene, which is vaporized and carried into the combustion tube, where it is burned by a ring furnace in a stream of 99.99% pure oxygen. The combusted gases are passed through hot copper oxide, a silver furnace and KMnO_4 traps, after which water is removed in a dry-ice trichloroethylene trap. The CO_2 is frozen down in liquid nitrogen. To obtain enough CO_2 to make 15 ml of benzene, it must burn for up to 4 h. A surge arrester (used in gas welding systems) is incorporated in the line to prevent a blow-back into the benzene. We also make sure that large volumes of benzene vapor do not accumulate before the benzene ignites.

VARIATION OF BACKGROUND WITH CO₂ VOLUME

Two spectrophotometric benzene (clean-out) samples were converted to remove memory effects from the synthesis rig. Subsequently, nine samples of spectrophotometric benzene were burned and reconverted, and each was counted for a minimum of 8000 min. The spread in the results was greater than expected from Poisson counting statistics alone. Subsequent analysis showed an inverse relation between the length of time for which samples were combusted and the background level. If modern CO₂ was present in one of the carrier gases, then one would expect an increase in background count rate for longer combustion times. As this did not occur, we ruled out CO₂ contamination from laboratory gases as a contributor to elevated background levels. Further analysis showed a relation between volume of CO₂ used for the lithium reaction and the background level (Fig. 2). In Belfast, we use identical-sized billets of lithium (*ca.* 90 g) for each

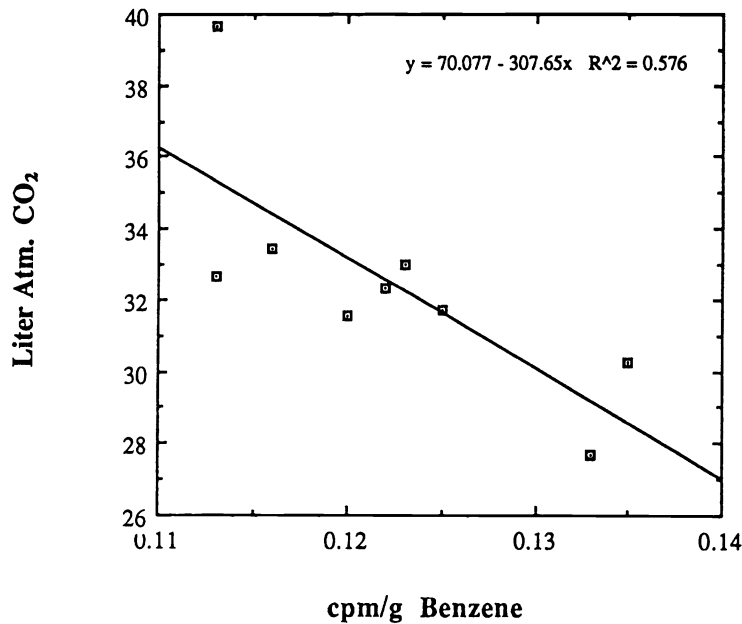


Fig. 2. Relation between background cpm and volume of CO₂ (liter-atm) reacted with a 90-g billet of lithium

reaction, which gives a variable excess of lithium for the reaction (Pearson 1983). However, as we have shown, the CO₂ volume reacted with a billet of lithium can vary between 30 and 40 liter-atmospheres, depending on the sample size (Fig. 2). This introduces variability in the synthesized background level because a constant amount of carbon is being added to a varying quantity of gas. The results shown in Figure 2 suggest that a constant stoichiometry should be maintained between lithium and CO₂ (including any excess lithium), as is the Tucson practice. Variations in the carbon content of the lithium will result in increased background variability even when constant stoichiometry is maintained.

MEMORY EFFECT AND VESSEL BACKGROUND CONTRIBUTION

To investigate memory characteristics of the lithium reaction vessel, we synthesized benzene from a sample of ANU sucrose (20.423 dpm gC⁻¹, determined from a consensus value of 150.61% modern carbon (pMC) (Rozanski *et al.* 1991)). We followed this sample with the conversion of 5 spectrophotometric benzene samples, combusted in the manner described above, to produce *ca.* 16 ml of benzene for each. These were counted for a minimum of 8000 min. Figure 3 shows the

results. The first two samples converted after the ANU sucrose show a memory effect that levels out at the third conversion. The count rate at which the leveling out occurs is at 0.008 cpm g^{-1} above the count rate of the original spectrophotometric benzene that has not been burned and re-converted. This experiment has been repeated several times (Long & Kalin 1992) and the cpm of the burned benzene always exceeds that of the original material, yielding a value less than that of benzene derived from anthracite.

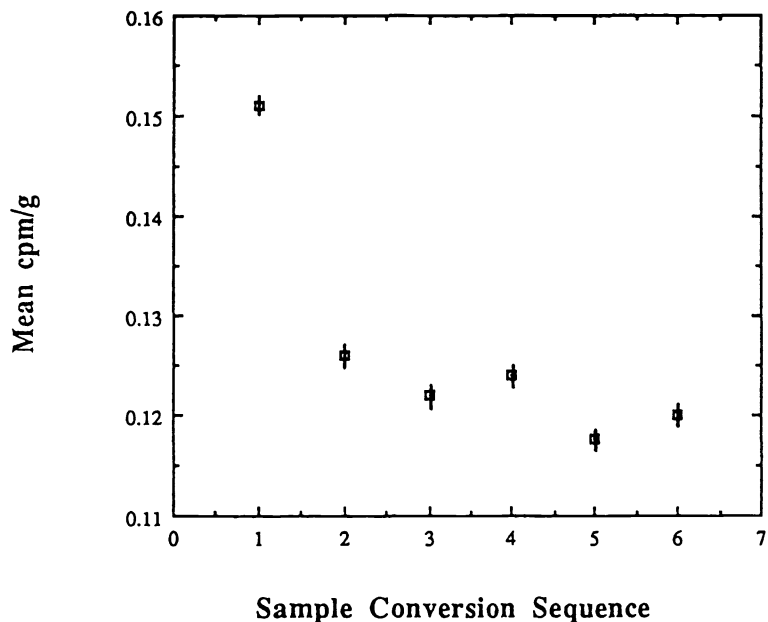


Fig. 3. Successive cpm levels after conversion of a sample of ANU sucrose ($20.423 \text{ dpm gC}^{-1}$) for back-burned spectrophotometric benzene. Count rate stabilizes after the conversion of two "dead" carbon samples. Error bars are ± 1 standard deviation (1σ). Instrument background has not been subtracted from the results.

The nominal carbon content of Type 304 stainless steel is 0.08%. To add 0.008 cpm g^{-1} at 66% counting efficiency would require the addition of *ca.* 11 mg of modern carbon to our samples. Because anthracite is used as the carbon source in the production of steel, it is highly improbable that additional activity (after the memory of samples that contained ^{14}C is removed) is added from the steel. Also, if all the carbon required to account for the additional activity were supplied by the vessel wall, then $20 \mu\text{m}$ of surface erosion would have to occur each time a sample is converted, assuming that only the bottom 25% of the reaction vessel donates carbon. This is excessive, and would result in a thinning of the wall from the inside of about 10.0 mm during a vessel's life. Gurfinkel (1987) discussed contamination from a small Type 304 stainless steel reaction vessel used for converting samples for accelerator mass spectrometer (AMS) dating. Gurfinkel showed that 0.2% of the acetylene yield of normal AMS samples (*ca.* 4 mg carbon) could be generated from within a thoroughly cleaned furnace without the addition of CO_2 , and suggested that the vessel wall or lithium metal was the source of carbon. About $8 \mu\text{g}$ of carbon are required to generate this quantity of acetylene, which, when scaled up to the larger sample sizes used in liquid scintillation counting (LSC), is equivalent to 26 mg of carbon in a 13-g sample. This is well in excess of the modern carbon yield of lithium, and suggests a "dead" component in the lithium source and from the vessel wall. Because the surface-area-to-volume ratio of the small reaction

vessel used to produce AMS samples would attenuate the effect of carbon donated by the vessel wall, we could expect the scaled-up figure of 26 mg to exceed that observed in the larger systems if the vessel is providing carbon. Experiments performed both in Belfast and Tucson in which synthesis was attempted without adding CO₂, showed a carbon yield in excess of the levels required to account for residual activity. This yield was below the level of Gurfinkel's (1987) scaled-up figure, which suggests that the vessel provides some of the "dead" carbon. Thus, vessel size and construction material introduce two more sources of background variability. However, given that the reaction vessel will be the same within each lab, the overall effect on variability should be minimal.

LITHIUM METAL AS A SOURCE OF ¹⁴C CONTAMINATION

Two sources of carbon contamination may be introduced during lithium metal manufacture: 1) graphite rods used to plate out the lithium metal ("dead" carbon) and 2) lithium oxides, lithium hydroxides and lithium carbonate from exposure to air during manufacture and laboratory use. The graphite for these rods is usually of geologic origin; therefore, even if there are small flecks of graphite in the lithium, sample activity would be diluted. When exposed to air, lithium reacts with atmospheric CO₂, forming lithium carbonate. This carbonate has a modern ¹⁴C signal and can be a source of contamination. To test this possibility, we heated lithium metal in the reaction vessel to 600° C to form lithium carbide with any carbon present in the system. After cooling, the lithium was hydrolyzed routinely and the residual acetylene collected. This process produced *ca.* 11 mg of carbon as acetylene. The count rate of the synthesized samples above the spectrophotometric benzene suggests that 10.8 mg of modern carbon are needed to increase the synthesized benzene above the spectrophotometric background count rate. Therefore, it seems likely that lithium is the primary source for ¹⁴C in the synthesized backgrounds. The lithium that Long and Kalin (1992) used was specially chosen for low carbon and nitrogen content. Low values of both of these suggest very little exposure to the atmosphere. Hence, their value for added ¹⁴C is 2.8 mg of modern carbon equivalent. Consistency in the level of impurities in the lithium is essential for near-background dating; Long and Kalin (1992) have adopted a policy of testing each batch of lithium and selecting the batch with the lowest carbon content. Careful control of the stoichiometry of the Li-CO₂ reaction is needed to ensure that the chemical blank from this source of contamination remains constant, as discussed above.

The count rate produced by the synthesized benzene after memory effects have been removed defines the minimum background attainable. Carbon added at the pretreatment stage, or present as a contaminant in background material, would raise the background further. Studies we performed in Belfast using 125 ka subfossil wood from the Eva Forest bed in Alaska (collected and submitted by Troy Pewe, Arizona State University, Tempe, Arizona) showed no evidence of contamination at the cellulose extraction stage (Pearson 1983) because the count rates from the Eva wood are identical to those from back-burned spectrophotometric benzene. Significantly, Long and Kalin (1992) use ethanol (manufactured by a fermentation process) in their pretreatment process; this seems to add a small modern carbon component. The Belfast lab does not use ethanol in the pretreatment of wood.

OPTIMIZATION OF ¹⁴C COUNTING WINDOW FOR LOW-ACTIVITY SAMPLES

Stability of the LS counter is very important when attempting to measure small amounts of ¹⁴C; chemical blank background must be counted for up to 70 days, and each sample for a minimum of *ca.* 9 days (13-g samples). Different instruments and laboratories each have different background spectral characteristics, and one must characterize each instrument in its working environment to

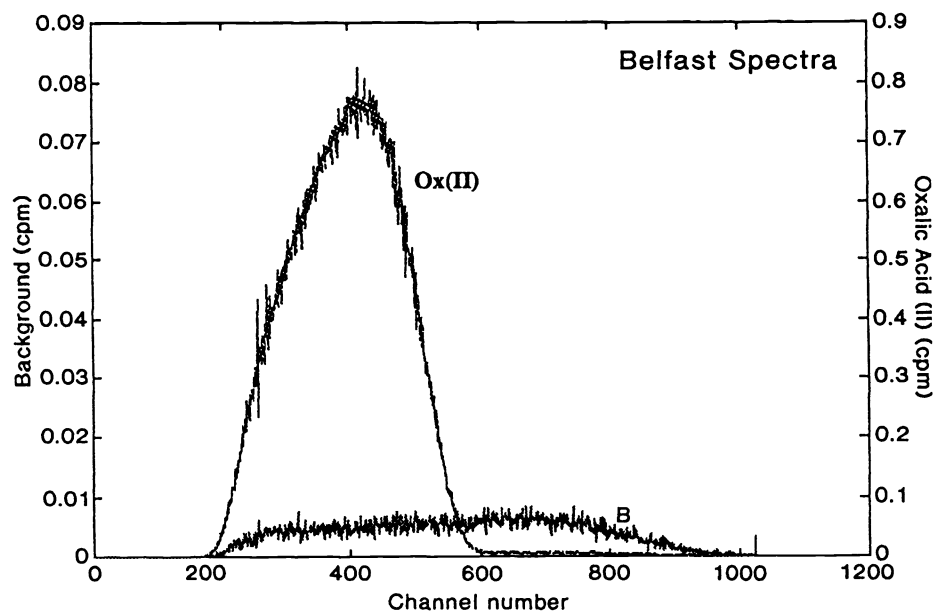


Fig. 4. Quantulus #2: Queen's University of Belfast, NIST Oxalic Acid II ^{14}C spectrum and spectrophotometric benzene background spectrum

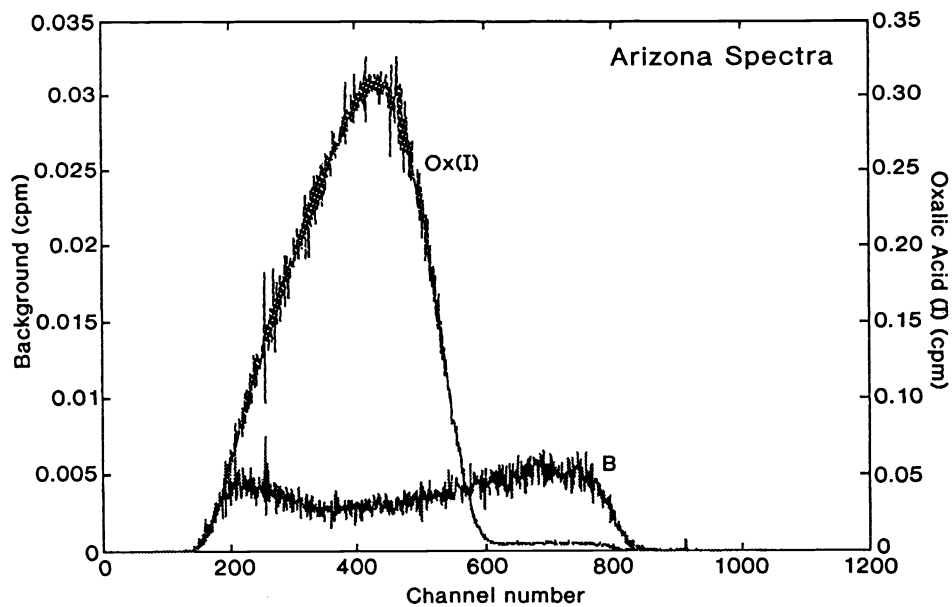


Fig. 5. Quantulus #4: University of Arizona, NIST Oxalic Acid I ^{14}C spectrum and spectrophotometric benzene background spectrum

ensure optimization. To study these parameters, we chose two Wallac 1220™ Quantulus counters used for measurements of very low-activity samples, one at the Queen’s University of Belfast and the other at The University of Arizona. The instruments at both laboratories are housed in specially designed low-level counting facilities. The Belfast counting laboratory has 1.6 m of low-activity concrete shielding and strict environmental control. The Arizona laboratory has 10 m of shielding and, again, strict control over environmental parameters (Kalin & Long 1989). Both instruments were modified so that manual control of the voltages applied to the photomultiplier tubes (PMTs) was possible. We determined the optimum operating voltage for both instruments, as described by McCormac (1992). Figures 4 (Queen’s University of Belfast) and 5 (University of Arizona) show the spectra obtained using NIST standard oxalic acid and background benzene. The oxalic acid spectra are very similar but the backgrounds are quite different; this is due partly to the use of different materials in successive generations of the same instrument and to the different locations of the instruments. Nonetheless, Figures 4 and 5 show that, with such variability in the spectral form of the background, one must optimize each instrument individually.

The optimal window settings for detection of very low-activity samples must allow for both the maximum stability of both the ¹⁴C spectrum (*i.e.*, operation at balance point) and the background count rate. This window depends heavily on the spectral characteristics of each instrument. To optimize the parameters, we used the technique described by Polach *et al.* (1983) and McCormac (1992), in which a soft window, of variable width, is passed over the background and standard spectra. Figure 6 shows the results for the Queen’s University of Belfast data, and Figure 7, for the data collected at The University of Arizona. The peak count rate for a given ¹⁴C counting window defines both the lower discriminator level and the window width for balance-point operation. Balance point, however, is not necessarily the point at which the figure of merit ($FM = E^2/B$) is maximized, because the background may not be a minimum at this point.

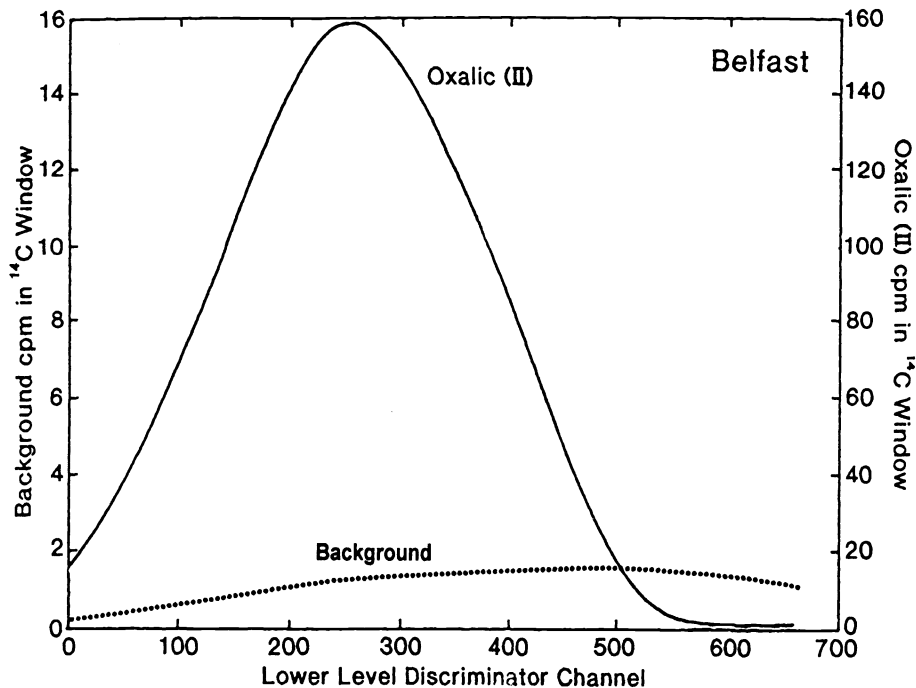


Fig. 6. Window optimization of ¹⁴C count rate and background for Belfast Quantulus #2 counter

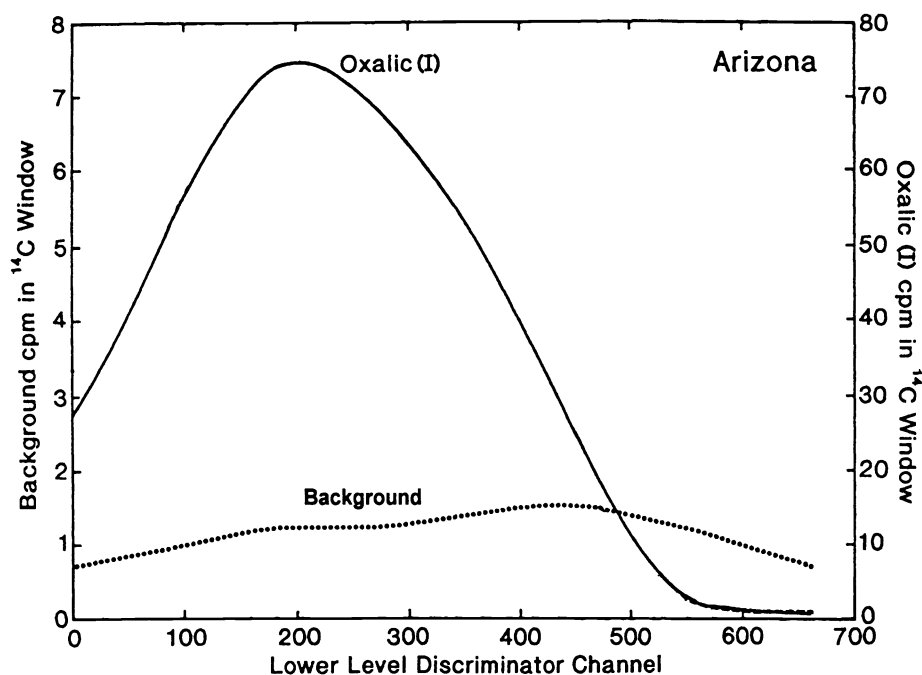


Fig. 7. Window optimization of ^{14}C count rate and background for Arizona Quantulus #4 counter

However, by altering the window width, it is possible to find an optimum window width and lower-level-discriminator (LLD) value that yield a balance point at a position where the rate of change of background within the ^{14}C counting window is minimum. Laboratories with no ^3H in the water used for acetylene synthesis (*e.g.*, Arizona) can experiment with a wide range of window settings, whereas in Belfast, our LLD range, and hence window width, is limited by the presence of ^3H in our water supply. Nonetheless, small alterations can be made to improve both the FM value and variability in background as a spectrum moves in response to instrument gain changes. Optimizing an instrument in this way will result in background variations of a few 10,000ths of a cpm in response to small shifts in the sample spectrum.

CONCLUSIONS

The measurement of very low-count-rate samples for ^{14}C dating requires a complete understanding of the potential sources of contamination as well as extreme stability in the LS counting equipment. Our findings in this study show that:

1. A constant stoichiometry needs to be maintained between the lithium and CO_2 used in the acetylene synthesis process.
2. Memory effects in the reaction vessel are negligible after three successive background samples.
3. No detectable ^{14}C activity is added during the combustion of the sample from laboratory gases.
4. Additional modern ^{14}C is added to the sample in the lithium reaction line. We speculate that lithium contributes most of this modern contamination, possibly as lithium carbonate forms when lithium metal reacts with atmospheric CO_2 .

5. The ¹⁴C counting window for measuring very small amounts of ¹⁴C activity should be at balance point, and chosen so that small changes in instrument gain have a minimal effect on sample and background count rates. Computer software can enable convenient scanning through many possible window settings to produce a balance point for ¹⁴C counting and optimal FM.

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