

Chapter 10

Liquid Scintillation Counting of Low Levels of Carbon-14 for Radiocarbon Dating

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INTRODUCTION

Before describing the preparation and measurement of samples I shall attempt to indicate the purpose of this work by outlining briefly the principles of radiocarbon dating.

The possibility of radiocarbon dating by measurement of naturally occurring carbon-14 was first suggested about 1949 by W. F. Libby and his co-workers at the Institute for Nuclear Studies, University of Chicago.^{1,2} Earlier work by Korff and others some years previously had shown that secondary neutrons are produced in appreciable numbers at a few miles altitude in the Earth's atmosphere by the action of primary cosmic radiation. From consideration of a number of possible nuclear reactions which might occur involving these neutrons, Libby concluded that the relatively long-lived radioactive isotope carbon-14 would be continuously produced in small amounts as a result of neutron capture by ordinary stable atmospheric nitrogen-14. He predicted that the carbon-14 atoms formed in this way would be rapidly oxidized to carbon dioxide which would become mixed and uniformly distributed by atmospheric circulation and exchange processes in a short time in comparison with the average lifetime of a carbon-14 atom of about 8300 years, so that an equilibrium would be established between the atmosphere and ocean water and the biosphere such that the rate of production of carbon-14 would equal the loss from the system by radioactive decay.

The mechanism by which the cosmic ray-produced carbon-14 is oxidized to carbon dioxide before entry to the exchange reservoir is still imperfectly understood although various processes have been suggested.³ However Libby showed first, using an isotopic enrichment process, that carbon-14 is present in the biosphere in detectable amounts and secondly, by measuring modern living material from different locations on the Earth's surface, that essentially uniform global mixing does occur. Natural carbon-14 was found to have a low specific activity of the order of 7×10^{-12} Ci/g of carbon so that only a very small proportion of atmospheric carbon dioxide is labelled with carbon-14.

Carbon-14 enters the biosphere during photosynthetic uptake of atmospheric carbon dioxide by green plants. Because such plants are at the base of the food chain, all living organisms are theoretically in radiocative equilibrium with atmospheric carbon-14. When an organism ceases to exchange with the carbon-14 reservoir at death, then disregard-

ing here the possibility of subsequent physical contamination by material of different age, the only way in which the incorporated carbon-14 activity can be altered is exponentially with time by radioactive decay. From a knowledge of the length of the half-life (taken as 5570 ± 30 years) and the so-called contemporary assay, and by measuring the activity remaining in once living samples such as wood, charcoal, bone, etc., the time which has elapsed since exchange ceased can be readily determined with reasonable accuracy.

There are, of course, uncertainties in the interpretation of whether the age obtained for the sample really dates the particular context from which the sample came but this is largely dependent on careful selection of material for measurement and is outside the scope of the present discussion.

After some twenty years the general validity of the carbon-14 dating method has not been seriously challenged, although there have been a number of severe practical and theoretical difficulties such as those relating to the establishment of a suitable modern reference standard due to the diluting effect of large scale combustion of fossil fuel over the last 150 years, accurate determination of the half-life of carbon-14, isotopic fractionation effects in nature, and more recently the realization that there have been fluctuations in the rate of carbon-14 production, so that for some periods in the past, carbon-14 years are not equivalent to solar years.⁴ Although the relative sequence of radiocarbon dates is still correct, many important archaeological chronologies cannot be absolutely dated until there is an adequate means of correcting for these past fluctuations and several laboratories are currently devoting much effort to the elucidation of this.

The most important practical requirement for radiocarbon dating is still measurement of the very low activity levels involved with sufficient accuracy – ideally to better than 1%, which is equivalent to ± 80 years – and which demands great stability of operation of the counting equipment over long periods. The sample for measurement must obviously consist of carbon in the most concentrated form which is practicable. Until fairly recently, because of the low energy of the carbon-14 β -particles, most radiocarbon dating measurements have been made by gas counting, usually with relatively large, low background proportional counters surrounded by an anti-coincidence counter arrangement and enclosed in massive steel or aged lead shielding weighing several tons. The central counter is typically filled with up to about 10 l of methane, acetylene or carbon dioxide at 2–3 atmospheres pressure, prepared from the original excavated sample material. Most of the eighty or so radiocarbon laboratories now operational still use the gas counting method, but laboratories being newly set up are now using liquid scintillation counting systems from the start and some older established laboratories, like ourselves, have adopted liquid scintillation counting to replace ailing conventional gas counter systems. Apart from the high figures of merit easily attainable, the attraction is largely that the automatic liquid scintillation counter enables frequent check measurements of the background and modern reference standard and known age samples to be made, so that the performance of the system can be closely and continuously monitored over the period during which the unknown samples are measured. This is not possible with a gas counter system in which sample changing is much less straightforward and background variations may be more critical. In other words, for low level work of the nature involved in radiocarbon dating, the safeguards afforded by liquid scintillation counting appear to be much better. There are a number of other important advantages, for example the scintillation system can be kept in continuous use whereas gas counters often require long periods for pumping out and refilling, during which time the electronic equipment is idle. The chemistry of sample

preparation for scintillation counting is generally more complicated but once satisfactorily prepared, the sample can be remeasured directly as many times as one may require and subsequently easily stored. Gas samples usually have to be repurified between each measurement and the time, effort and storage space involved is generally greater than for the more elaborate but single operation of preparing a sample for scintillation counting. Removal of radon, often present in the gas counting samples, is accomplished by storing the gas for about one month before counting, during which time the level of radon normally found in the samples decays to below detectable limits. Radon appears to be excluded during the synthesis of benzene for liquid scintillation counting so that no storage period is necessary before counting. Finally there is no need for the construction and support of the massive and costly shielding used to screen a gas counter system.

Earlier successful use has been made of liquid scintillation techniques for radiocarbon dating by a number of workers among whom Audric and Long^{5,6} used liquid acetylene; Barendsen⁷ used liquid carbon dioxide, Delaney and McAulay⁸ synthesized methyl alcohol and Tamers⁹ synthesized benzene using a diborane-activated catalyst. Generally because of various preparation hazards, low yields or lengthy catalysis times, none of these methods offered an attractive alternative to gas counting at the time. It was largely the work of Noakes *et al.*,¹⁰ who developed a much more convenient and effective vanadium-activated silica-alumina catalyst for trimerization of acetylene to benzene together with the improvements which had by then taken place in commercially available liquid scintillation counters, which led to a general renewal of interest in liquid scintillation counting among radiocarbon dating laboratories.

TECHNIQUE

The synthesis in use at the British Museum Research Laboratory is based on the large scale high-vacuum line preparation of acetylene from carbon dioxide via lithium carbide first developed by Barker¹¹ at the British Museum for gas proportional counting and later improved by him to give almost 100% yields of acetylene (Barker, unpublished work). A highly efficient silica-alumina catalyst is then used to convert acetylene to benzene for counting. All radiocarbon dating laboratories using liquid scintillation counting of benzene now follow the final version or minor variants of Barker's acetylene chemistry. Various detailed improvements have been made at the catalysis stage resulting in better yields of high purity benzene (judged mainly on quenching criteria although gas chromatographic analysis has also shown that only very small traces of impurities are present), greatly reduced risk of isotopic fractionation and reduction of the time needed for the catalysis.

Sample materials such as wood and charcoal and other plant remains are first pretreated with dilute acid and in some cases also with dilute alkali, for removal of possible contaminants accumulated during burial. All our samples are archaeological materials and usually will have been penetrated by carbonates or more recent organic substances (humic acids) transported by movement of soil water. To obtain a meaningful date these intrusive substances must clearly be removed as completely as possible. Bone and antler samples are demineralized with cold dilute hydrochloric acid at reduced pressure to remove the inorganic carbonate and phosphate components, leaving the protein (collagen) which has been found to be the most reliable fraction of these two materials (Krueger).¹² More detailed consideration of the complexities of sample pretreatment (Olson)¹³ would not be appropriate here.

After washing and oven drying, up to about 12 g of pretreated sample is ignited in a

silica crucible supported inside a 3 l stainless steel 'bomb' containing a suitable excess of pure oxygen, by passing an electric current through an element suspended in the crucible and covered by the sample. This combustion method is much more convenient and effective than the alternative large scale tube furnace (Barker *et al.*).¹⁴ As the bomb is filled to a pressure of about 10 atm with pure, aged oxygen, combustion is virtually instantaneous and generally little or no ash remains. The resulting gas mixture is pumped out with a large, 450 l/min, rotary pump, over a period of about 45 min, through a series of traps cooled with dry ice-acetone slush and liquid nitrogen for separation of water and carbon dioxide respectively from excess oxygen which is pumped away. Usually 12 g of pretreated sample materials will yield at least 9 l of carbon dioxide and this does not need to be purified before conversion to acetylene. For the age range normally expected 9 l of carbon dioxide will ultimately provide a large enough benzene sample to obtain an acceptably small associated probable error in one set of measurements. As the overall yield is predictable it is easiest to control the approximate final sample size at the start of the synthesis and any excess carbon dioxide over 9 l is generally not used. For samples which are too small to yield 9 l of carbon dioxide, the final benzene volume is made up to the standard 5.5 ml by adding 'dead' Analar benzene before mixing with scintillator solution. The volume of carbon dioxide obtained from the sample combustion is measured to determine the amount of lithium metal needed for formation of lithium carbide. Experience has shown that the highest yields of acetylene are obtained when 100% stoichiometric excess of lithium metal is used. After cutting a suitable quantity from an ingot kept under liquid paraffin, the surface of the metal is scraped to remove any carbonates and then washed with petroleum ether to remove oil residues. The lithium is then heated under vacuum to 650°C in a stainless steel furnace of 3 l capacity, with a Meker burner. Lithium melts at 179°C and at about this temperature occluded hydrogen is released and is pumped away. After about 10 min heating when the pressure in the system is about 10⁻² mm Hg, the furnace is closed off from the pumps and the carbon dioxide sample is slowly admitted over about 45 min, keeping the pressure at about 10 cm Hg and the temperature constant at 650°C. The temperature can be judged by the cherry red colour of the molten lithium when viewed under dim light through the glass inlet tube and with a little experience the reaction conditions can be controlled without difficulty. When all the carbon dioxide has been reacted, after a further period of pumping at 650°C, the furnace is allowed to cool to room temperature, usually overnight. Distilled water is then run in slowly to regenerate acetylene. The resulting mixture of acetylene, hydrogen from the excess lithium and water vapour is pumped through a series of cooled traps to strip out the acetylene, in a similar way to that outlined above for extraction of carbon dioxide from the combustion bomb. Under favourable conditions the yield of acetylene is consistently 98% and seldom falls below 96%. The acetylene is passed through two columns of glass beads coated with 50% w/v sodium hydroxide solution and syrupy *ortho*-phosphoric acid respectively, and through a number of dry ice-acetone traps for final drying and is then absorbed onto a vanadium-activated silica-alumina catalyst. Storage bulbs at several points on the vacuum line allow the synthesis to be interrupted at each main stage and there is usually a different sample at each of these points in the process at any one time.

The silica-alumina catalyst is a commercial product though it is not generally available and we have been fortunate to secure some years' supply of this material. The catalyst is in the form of semi-opaque spherical beads ranging in diameter from about 2 to 5 mm. These are activated by soaking for a few hours in a solution containing 10% w/v of vanad-

ium pentoxide in 100 vol hydrogen peroxide (both GPR grade) diluted approximately fourfold with distilled water. The beads are then drained, washed and oven dried. The vanadium pentoxide solution is quite difficult to prepare satisfactorily but can be re-used several times. Before use the catalyst is finally dried under vacuum at 300°C for about 1½ h. The tube in which the catalyst is finally dried before absorption of acetylene has been designed and constructed by N. D. Meeks for efficient heat exchange. Absorption of acetylene onto the catalyst tends to be exothermic but higher yields of benzene are obtained if the catalyst is kept at ambient temperatures during the absorption. The tube consists of a small double concentric cylinder some 15 × 4 cm with the walls, which are about 1½ average bead diameters apart, sealed at the bottom and joined at the top to an inlet tube having a detachable high-vacuum stopcock. Construction of the tube is difficult but it is extremely efficient and quite robust. The catalyst is held in a thin layer in the annular space between the walls of the tube and the whole assembly is cooled with running tap water. 5 g of activated catalyst are used per litre of acetylene. Initially the acetylene absorption is very rapid but as the pressure falls below about half an atmosphere, the rate of uptake decreases until finally after about 1½ h there is a residual pressure of 6 to 8 cm which is a low percentage loss as the dead volume of the manifold is small. If the acetylene pressure is raised to 1 atm or above benzene 'rains' from the catalyst onto the cooled tube walls. However, our attempts based on this and similar observations with other catalysts, to construct an apparatus in which acetylene absorption and benzene recovery are simultaneous have so far proved to have no advantages in time saved or higher benzene yields.

Benzene is recovered by heating the tube to 150°C in a tube furnace, the desorbed benzene being collected in a liquid nitrogen cold finger. Approximately 85 to 90% of the available benzene is desorbed in the first 10 min but to achieve the minimum acceptable yield of 95% heating must be continued for at least 1 h.

The catalysis mechanism is probably that gaseous acetylene molecules become attached to the catalyst and polarized, and other acetylene molecules link with these until, when three are attached, the benzene structure is formed by angular rotation (Noakes *et al.*).¹ Conversion of acetylene to benzene is most probably almost quantitative but, probably due to the large surface area of the catalyst (450 m²/g) complete benzene recovery is not possible. A semi-micro combustion apparatus was constructed for the quantitative re-conversion of benzene to carbon dioxide so that mass spectrometric measurements of the carbon-13/carbon-12 ratios could be made for comparison with the carbon-13/carbon-12 abundance ratios of the bomb carbon dioxide from the initial sample combustion. Re-conversion of benzene to carbon dioxide was necessary for this comparison due to the irregularity of the cracking pattern of benzene in the mass spectrometer. Measurements made on a considerable number of samples over a period with an AEI MS 20 double collection mass spectrometer have shown that no significant fractionation occurs during the synthesis of benzene although the overall yield from carbon dioxide to benzene may be as low as 92% theoretical. This also has the practical advantage that, for the routine correction of dates for isotopic fractionation in nature, a mass spectrometer sample can simply be taken from the bomb carbon dioxide and it is not necessary to reconvert an aliquot of each benzene sample synthesized.

The activated catalyst is yellow-brown in colour but becomes black after use probably as a result of slight reduction of vanadium (P. R. Mitchell, personal communication). It is possible to re-use the catalyst but this is not done to avoid any cross-contamination of samples arising from memory effects.

At the end of the benzene recovery period dry air is admitted to the collection manifold and the benzene is allowed to warm up to room temperature. The collection tube is then detached from the vacuum line and the benzene is poured into a tared counting vial for accurate weighing. The preferred sample size is 5.54 ml, corresponding to 4.86 g of benzene. Samples smaller than this are made up with 'dead' benzene to 5.5 ml. 9.5 ml of scintillator solution consisting of PPO in scintillation grade toluene is added, to give a final concentration of PPO equivalent to 4.0 g/l and total sample volume of 15 ml. No wavelength shifter is added and the samples and scintillator solutions are handled in ordinary air. Flushing with an inert gas does not appear to be necessary and would probably cause unacceptable evaporation losses with little improvement in quenching. Standard low potassium glass counting vials with plastic caps lined with cork-backed foil are used. A group of these having comparable backgrounds has been laboriously selected and these same vials are re-used continuously with occasional replacement of the caps. There would be some advantage in using lower background quartz vials but none of those available have closures which will satisfactorily prevent evaporation losses. Plastic vials which might be better still are not sufficiently resistant to the toluene-benzene samples over the long counting periods necessary although the possible use of some newly available plastic vials is being investigated.

The samples are counted in a Model 3315 Packard Tricarb liquid scintillation spectrometer having selected quartz-faced photomultiplier tubes (EMI 6255B), AES and teletype output. With the high voltage, gain and window settings used, the efficiency to an unquenched carbon-14 standard of known activity is about 66% and the efficiency to tritium is negligible. This is important because the distilled water used to generate acetylene from lithium carbide is derived from London tap water which is not tritium-free so that there is a level of tritium in the samples of approximately the same order as the expected carbon-14 activity. The operating temperature is 0°C and there are no measurable evaporation losses from the samples over a period of several weeks at least.

Samples are counted, usually for one week, in groups consisting of a sealed, unquenched carbon-14 standard, modern reference standard, background, sealed known age sample and a group of three or four unknowns. Apart from the 'hot' carbon-14 standard which is stopped by a preset count of 900000 after about 13.75 min, at least fifteen individual counts of 100 min each are accumulated for all samples in the group.

External standard channels ratio quench measurement is made at the end of each week's run to avoid additional background variations due to imprecise repositioning of the AES source if this is repeatedly moved while sample counting is in progress. There is only a few per cent of quenching and although the samples do not vary greatly and there would be a slightly lower background with the AES source removed, lack of correction for quenching could introduce age errors of perhaps 40 years which is of the same order as the precision of measurement attainable. Old or small samples do not provide enough carbon-14 counts to permit reliable quench correction by internal channels ratio.

The particular background accumulated each week is used for that week's counting only because, although there is little variation from the nominal background of 7.7 counts/min, changes of 0.1 c.p.m. are important when unusually old or small samples are being measured. In an eight-sample group counted for one week, about 12000 background counts and up to about 50000 net counts for each sample are accumulated, depending on the size and age of the samples. The upper detectable age limit is about 45000 years before present (B.P.) although this could be extended by at least one half-life by increasing the amount

of benzene but keeping the total sample volume constant. Performance of our Tricarb, which is used exclusively for radiocarbon dating, has been extremely stable and practically free from faults over a period of five years and although the gain settings are checked every week the balance point seldom requires any adjustment at all.

A matrix of data in the form of eight-track punched paper tape comprising sample identifications, accumulated counts, quench data, benzene weights and isotopic fractionation values is processed each week by University of London Atlas Computing Service using an Algol program written for us by A. J. Barker of King's College, London which is stored on magnetic tape. The print out gives a complete statistical analysis of the count data, a number of parameters needed for monitoring system performance and the calculated sample ages and associated age errors. At present no data are permanently stored in the computer. Usually the results are available within a day and the cost of computation is very modest.

Most of our work is related to the research programmes of the British Museum's own Antiquities Departments and is concerned largely with the dating of prehistoric cultures of the British Isles, parts of Europe and some other areas, and investigation of carbon-14 reservoir fluctuations back to 3000 B.C. using closely dated material from Egyptian and other well documented contexts. Special projects in human palaeontology, dating the extinction of post-Pleistocene mammals, comparisons with other dating methods such as thermoluminescence and some fundamental work on carbon-14 dating problems, are also in long-term progress. About 150 to 200 samples are dated in a year and the results are published periodically in the journal *Radiocarbon* and some also appear in articles in various leading archaeological journals.

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No work of this kind is possible without a team effort. We are indebted to Mr. H. Barker under whose direction the dating work is carried out, for much helpful criticism and guidance. Mr. N. D. Meeks has skillfully constructed much of the glass high-vacuum system and painstakingly synthesized hundreds of benzene samples. More recently Miss M. A. Pulle has also synthesized samples and both of them have read and commented on this paper. Mr. A. J. Barker has been to much trouble to write a comprehensive Algol computer program for us. We are also indebted to our colleagues in other departments of the British Museum and elsewhere for advice on many matters relating to the dating work.

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DISCUSSION

P. Stanley: Since the counting period is so long is the evaporation of your scintillator solution significant?

R. Burleigh: Our counter is operated at 0°C and we have shown by careful periodic weighing of samples that evaporation losses are very small – a few milligrams over a period of several months if the vial caps are tightened up well. There is no measurable loss of scintillator solution at all over the normal counting period of 1 to 2 weeks.

P. Stanley: Do you employ 5 ml vials attached to an optically dense plastic base to cut down optical cross talk between the photomultiplier tubes or do you employ conventional sized vials?

R. Burleigh: Standard 20 ml low potassium glass vials selected for comparable backgrounds and containing a total volume of 15 ml of scintillator solution are used. The walls of the horizontally opposed photomultiplier tubes are optically masked from each other.

P. Stanley: Do you use a reduced high voltage supply to the photomultiplier tubes and operate at balance-point settings?

R. Burleigh: The high voltage supply to the photomultiplier tubes has been reduced by several hundred volts below the factory optimized setting for tritium. This has been done principally to minimize the background (which comes down to about 7.7 c.p.m. with selected quartz face photomultiplier tubes) but also eliminates possible interference from any tritium introduced during the benzene synthesis. Under the operating conditions used there is negligible efficiency to tritium and about 65% carbon-14 efficiency at balance-point settings giving a figure of merit of about 600 – a great improvement on the performance of most gas proportional counters used for radiocarbon dating.