Critical Assessment of Radiocarbon Dating

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Critical assessment of radiocarbon dating

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In applying physicochemical techniques of analysis to archaeological problems, the difficulties arise from two main sources: the equipment and the customers. On the one hand there is a continuing need to keep abreast of new developments in techniques of examination, and on the other hand the problem of communication and collaboration with specialists in disciplines which have little in common with physics or chemistry. Throughout the years, the Research Laboratory of the British Museum has developed some expertise in both these fields, but nevertheless radiocarbon dating taxed its resources to the limit. As a problem in analysis it is formidable—the task involves the measurement of levels of concentration many orders of magnitude lower than the most sensitive chemical techniques. As a problem in communication there are also formidable difficulties involving concepts which do not arise in connexion with the application of other techniques of examination. Some of these difficulties have now disappeared with the introduction of improved techniques, others are inherent in the method and must be endured, and others, despite all the efforts made to avoid them, arise out of interdisciplinary misunderstandings. It would seem therefore to be an appropriate time to take a critical look at radiocarbon dating in terms of its effectiveness as a tool for archaeological investigations. In doing so I shall be speaking from the viewpoint of a laboratory which uses the technique along with many others almost exclusively in the service of archaeology.

The main criticisms and difficulties which one encounters in the operation of a dating laboratory are concerned with *accuracy and reliability, the interpretation of results* and the *limited facilities available*. This last of course is related to the high cost of the operation.

Accuracy

It is over questions involving the accuracy of radiocarbon dates that most archaeological criticism of the method has arisen and indeed still arises. This is not altogether surprising for the advances of the past two decades have introduced more complexities than they have resolved. Consequently, if one is asked by a layman to state the accuracy which can be achieved at the present time, any attempt at a precise answer must be so hedged around with qualifications as to appear deliberately evasive if not downright shifty.

At the outset, one is faced with the difficulty that the estimate of the accuracy of a published date, the so-called 'error term' relates only to the measurements made in the laboratory and so does not take into account all the factors which may influence the accuracy of a radiocarbon date. The reasons for this are perfectly valid, for the errors it encompasses are the only ones capable of strict mathematical treatment and interpretation. In the early history of radiocarbon dating, the error term was a major source of misunderstanding since most archaeologists were unaware of its significance as a standard deviation and simply assumed that it defined a zone in which the true age must necessarily lie. Nowadays it would seem that most users of radiocarbon dates have grasped the necessary statistical concepts and learned to interpret the error

term correctly as defining a zone in which there is a 66 % (approx.) probablity that the true age lies. However, because of the emphasis placed on the importance of the error term, there is a tendency to overlook the other factors which can also influence the accuracy of radiocarbon dates. One reason for this may lie in the fact that initially, the statistical errors of measurement were by far the largest sources of error. Nowadays, the technique has improved to such an extent that this is certainly no longer the case. Consequently it is much more important that these other factors are now taken into account, particularly when the highest possible accuracy is required.

The half life of radiocarbon

The absolute value of a radiocarbon date depends on the value of the half life of radiocarbon used in the calculation of age. One is often asked why it is that dates are still calculated and published in terms of the original Libby value (5568 ± 30 years, Libby 1949) when more recent and presumably more accurate values are available. This question was debated at the Cambridge radiocarbon conference in 1962 and the reasons are clearly stated in a report in *Nature* by Professor Godwin later that year (Godwin 1962). Very simply it ensures uniformity and avoids even greater difficulties and confusion which would arise if one adopted each new value of the half life as it became available. In comparing two radiocarbon dates, the actual value of the half life is unimportant so long as the same value has been used to calculate both dates. However, where the highest absolute accuracy is required as, for example, when comparing radiocarbon dates with calendar dates, the most accurately known value of the half life should be used and the statistical uncertainty of this value must be included in the calculation of the error term.

Reservoir fluctuations

The absolute accuracy of a radiocarbon date is also influenced by the existence of fluctuations in the level of radiocarbon in the carbon exchange reservoir in the past. The existence of these fluctuations was first pointed out by de Vries (1958) and many workers, notably Suess, have since contributed to our knowledge of this phenomenon (Willis, Tauber & Munnich 1960; Ralph & Stuckenrath 1960; Suess 1965; Damon, Long & Grey 1966; Stuiver & Suess 1966; Ralph & Michael 1967; Suess 1968). The subject has already been dealt with in detail by other speakers and I propose only to point out the main implications of these fluctuations in so far as they affect the accuracy of radiocarbon dates. These are:

(*a*) In certain regions of time there are quite large differences between the radiocarbon ages and the calendar ages of materials. If a problem demands close comparison with calendar dates then an appropriate correction based on these recent researches must be applied to the radiocarbon date.

(*b*) In certain parts of the time scale, it is impossible to resolve fine detail by the radiocarbon method because samples from these parts will have the same radiocarbon assay although they are of different chronological age.

Isotopic fractionation in nature

Another source of some confusion to the archaeologist in connexion with radiocarbon dates is the application of isotopic fractionation corrections. The need to allow for the effects of isotopic fractionation in nature by applying a correction to radiocarbon dates based on mass

spectrometric measurements of the other carbon isotopes, carbon-13 and carbon-12 was first pointed out by Craig (1953), and since that time many laboratories have adopted this refinement as a routine measurement. The error introduced by isotopic fractionation effects is usually quite small, amounting on the average to no more than ± 80 years, and a number of laboratories without facilities for making the necessary measurements of isotope ratios have allowed for the possible error by widening the limits of the published error term. This certainly prevents the user of the dates from taking too optimistic a view of the figures, but on occasion the error can be much larger than the average as is demonstrated in table 1 where it can be seen that the correction produced a difference amounting to more than 200 years. Thus where the highest accuracy is needed there is no alternative but to make isotopic fractionation measurements and to apply the appropriate corrections.

THE SAMPLE AND ITS ENVIRONMENT

I would like now to consider the errors associated with the sample and its environment.

(i) *Archaeological context.*

The first and major point which must be considered is the archaeological context of the sample. The date derived from the sample relates to the death of the organism from which the sample is derived. Usually this is not the event in which the archaeologist is interested. Therefore it is very important that this difference is kept in mind when selecting material for dating. Unless it is possible to infer a close relationship in time between the two events a large and indeterminate error is introduced and the efforts of the dating laboratory are to a large extent wasted. This consideration also has a bearing on the type of material selected for dating. In the case of animal remains such as bone and skin products, and vegetable remains such as cloth, reeds and charcoal from young brushwood, it is usually possible to infer the necessary close relationship in cases where high accuracy is required. However, when selecting wood and charcoal from massive timbers, one must bear in mind that there can be several hundred years difference in age between the heartwood and the cambium of some trees. In this case one must not only establish a close relationship between the felling of the tree and the event of interest but also the position of the sample relative to the outer rings in the tree ring sequence.

(ii) *The nature of the sample*

The chemical nature of the sample also has a bearing on the accuracy of a date since it determines the extent to which chemical treatment can be used in the laboratory to remove non-contemporaneous materials such as humic acids and rootlets with which the sample may have become contaminated during its period of burial in the ground. Hard charcoal is perhaps the safest material in this respect since its stability to chemical attack enables one to adopt quite drastic procedures to remove such contamination. Unfortunately many samples classed as charcoal are not much more than very slightly charred or merely heavily degraded wood and cannot be treated in this way. In these cases rootlet penetration can produce highly erroneous results for it is exceedingly difficult to remove completely by hand sorting. The effect of such contamination can be seen in table 2 which compares two samples from Hod Hill, one heavily contaminated with rootlets and the other carefully selected by hand sorting in the laboratory to be free from such contamination.

Bone and antler acquired a bad reputation in the early days of radiocarbon dating. There is

no doubt that the use of whole bone or antler without chemical pretreatment is fraught with some considerable risk of error arising from chemical exchange of carbon between the inorganic carbon of the bone and that of the environment in which it was buried. Inorganic carbonates laid down in the bone or antler structures during burial can also produce erroneous results unless eliminated by suitable chemical treatment. This risk does not arise to the same extent if one restricts dating to the organic fraction of the bone or antler, and a number of laboratories have adopted procedures based on this reasoning (Munnich 1957; Olson & Broecker 1958; Barker & Mackey 1961). At the British Museum all bone and antler samples are completely demineralized before combustion, and from time to time we have been fortunate in securing material which allowed a close comparison to be made between bone and antler treated in this way and a more reliable material such as charcoal. Several such comparisons are listed in table 3. The first example, the antler from West Hartlepool is unique in that it was charred on the outer surface and thus provided a carbon sample to be set against both compact antler with a low surface to volume ratio which could be expected to give a reliable result, and spongy material with a high surface to volume ratio which should be subject in a much higher degree to the effects of organic contamination from the environment. The results of these various measurements support the view that properly demineralized *compact* bone and antler can give reliable results providing the material is sound and still contains a fairly high proportion of its original organic carbon.

It must be noted, however, that demineralization cannot ensure the complete removal of any organic contamination, e.g. humic acids, which may be present in the bone and this type of contamination can lead to errors particularly when the bone is in poor condition and contains only a small proportion of its original carbon.

This very brief survey of the main factors which can influence the accuracy of radiocarbon dates will perhaps serve to emphasize the need for a cautious approach when applying dates to archaeological problems, particularly when they have been abstracted from the literature rather than being obtained in collaboration with a dating laboratory. The published errors cannot take all the factors into account—indeed they may not necessarily have taken into account all those capable of laboratory assessment. For example it is not difficult to find examples in date lists of about a decade ago of dates published with error terms of perhaps ± 60 years or even smaller which relate only to the statistical error of measurement of the radio-activity of the sample. Such figures tend to give an entirely false impression of the real accuracy obtainable by radiocarbon dating and must be used with extreme caution. In addition, the nature of the sample and its archaeological context may introduce uncertainties which cannot be easily quantified. Thus the overall accuracy of a radiocarbon date depends as much on good archaeology as it does on the efforts of the dating laboratory. The effectiveness of the method in dealing with archaeological problems depends very much on the extent to which the archaeologist and the physical scientist understand the capabilities and limitations of each other's techniques. This underlines the need for effective communication between the disciplines. At the British Museum, the Radiocarbon Advisory Committee, formed at an early stage in the history of the dating unit, plays a vital part in this process providing, through the services of its members, a direct link with the archaeologist and a means of ensuring that the samples on which the laboratory operates are of the highest standards and are as far as possible unequivocal in their archaeological context. It also ensures that the available resources are exploited to the maximum advantage in investigating the most important archaeological problems.

The cost of radiocarbon dating

I now turn to the other main criticisms of radiocarbon dating which are all interrelated. *High costs*, *limited facilities* and *long delays* in the delivery of results.

The basic difficulty arises from the very low levels of radiocarbon in the samples and the properties of radioactive substances in general. The maximum level of radiocarbon involved is that in the 'modern' reference sample and is of the order of one part in a million million of ordinary carbon. This is a very much lower level than one meets in any other analytical problems and it is further complicated by the fact that one cannot measure even this level directly. Instead one has to infer its concentration from the rate at which it disintegrates, rather like trying to infer the total population of the British Isles from a consideration of the death-rate measured over a short period of time. In practice since one must cater for samples no larger than a very few grammes of carbon and since one has to accumulate at least 10 000 disintegrations in order to obtain a reasonable accuracy of measurement, it means that the measuring equipment is occupied for at least 24 h with each sample. This accounts to a large extent for the high cost of radiocarbon dates and would seem to rule out any chance of improvement. However there have in fact occurred some improvements in technique notably in liquid scintillation counting which do allow for a modest reduction in costs and also bring with them some other benefits.

The preferred method of measurements for the past 15 years and the method still in use in the majority of dating laboratories is proportional counting. In this technique, the carbon in the sample is converted into a suitable gaseous compound, usually carbon dioxide or a hydrocarbon gas such as methane or acetylene, and its radioactivity is then measured in a proportional counter. The technique has many advantages over the original solid carbon method and so over the years has come to be regarded almost as the only method worth considering when equipping a laboratory for radiocarbon dating. If one examines it critically, however, from the point of view of cost effectiveness, it does have one major disadvantage—the process of changing a sample is time-consuming and absorbs manpower. Moreover, during this period the counter cannot be used productively in measuring a sample and thus the equipment is not 100 % effective throughout the 24 h. Another disadvantage arising from this inability to change samples quickly, is that it is not possible to consider making frequent measurements of the background count rate of the equipment during the course of the measurement of a sample as was possible with the solid carbon technique. Since it is vital to know the exact value of the background, the alterative procedure has to be adopted of surrounding the counter with massive, elaborate and of course expensive shielding in order to ensure that the background count of the equipment is as low and as stable as possible and remains so over long periods of time. If these conditions are met it is reasonable to assume that the background count of the equipment has remained constant during the period of measurement of a sample. Note, however, that this *is* an assumption and in order to minimize the element of doubt associated with it, and for other reasons, it is usual to make at least two separate overnight measurements of a sample separated by a fairly long period of time during which at least one measurement of the background is made.

On the other hand, in liquid scintillation counting, the sample is converted into a liquid compound of carbon, and its radioactivity measured in a liquid scintillation spectrometer. The sample now occupies much less bulk than the corresponding amount of gas and can be

contained in a small glass vial. The measuring equipment is also correspondingly much smaller than that required for proportional gas counting and has the added advantage that it is readily available, since these instruments are made and sold primarily for purposes other than radio-carbon dating. In addition, as one might reasonably expect with instruments in quantity production, they do not suffer from a long period of 'teething troubles' when first installed as seems almost inevitable with most of the specially constructed equipment used for dating by proportional counting.
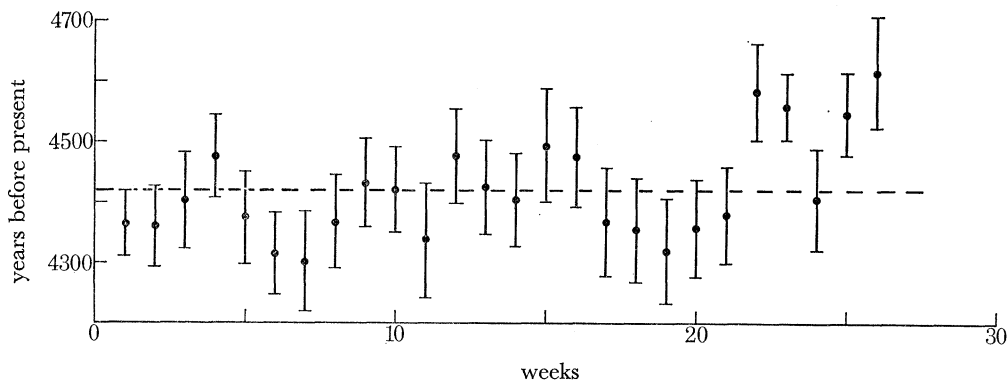

FIGURE 1. Results of replicate measurements, by the liquid scintillation technique, of a single sample over a period of 6 months.

The major advantage arising from the use of liquid scintillation counting however lies in the fact that these instruments are primarily intended to deal with large numbers of samples and so are fitted with very reliable automatic sample changers which reduce this process to a matter of a few seconds for each sample. Thus by the adoption of this technique one achieves a worth-while saving in manpower and also utilizes the counting equipment for 24 hours a day. In addition, the instrument can be loaded with a group of samples including 'background' and 'modern' reference samples and set to carry out measurements in rotation at frequent intervals. In this way the background count of the instrument can be monitored throughout the period of measurement of the samples and reference samples and one needs make no assumption con-cerning the long-term stability of the background. The statistical tests which can be applied to the data obtained from groups of samples measured together in this way serve to increase one's confidence in the results compared with the proportional counting technique, and the reliability and stability of the instrument is perhaps best illustrated by reference to the results of repeated measurements of the same sample over a period of 6 months (figure 1) in which it can be seen that the deviations of the results from the mean value are no more than one would expect to arise from consideration of the statistical properties of radioactive decay.

The potential advantages of liquid scintillation counting for radiocarbon dating were recognized many years ago (Arnold 1954) but the method was not generally adopted because of the difficulty of synthesizing a suitable liquid compound of carbon. Several laboratories, among them that at Trinity College Dublin (Delaney & McAuley 1959), demonstrated the feasibility of this approach to radiocarbon dating but the carbon compounds involved, usually methyl alcohol, did not possess ideal properties for scintillation counting and were not particu-larly easy to synthesize. The position changed dramatically with the work of Noakes and his colleagues on the development of improved catalysts capable of converting acetylene into benzene at room temperature with high yields (Noakes, Kim & Stipp 1965). The significance of

this development lay partly in the fact that benzene contains approximately 92 % carbon and is an ideal liquid for scintillation counting, and also in the fact that a simple and efficient method for the synthesis of acetylene for radiocarbon dating was already in existence. It was developed at the British Museum Research Laboratory some 16 years ago (Barker 1953).

The chemistry of the entire process is summarized:

$$\text{sample} \xrightarrow{O_2} CO_2 \xrightarrow{Li} Li_2C_2 \xrightarrow{H_2O} C_2H_2 \xrightarrow{catalyst} C_6H_6.$$

The overall yield of the synthesis is very high (92 to 95 % and mass spectrometric measurements have shown that the processes do not introduce any isotopic fractionation which might lead to errors in the resulting radiocarbon dates. It is interesting to note here in connexion with the cost of dating, that when the scintillation method was first adopted at the British Museum, the catalyst then available commerically (not based on Noakes's work) was only about 78 % efficient in converting acetylene into benzene. Moreover, 100 g were required for each litre of acetylene and the total cost of catalyst for each sample was nearly £2. We now produce our own version of the vanadium activated silica-alumina catalyst described by Noakes; this gives yields of benzene in the region of 98 to 99 %, and only 5 g are required for each litre of acetylene. The cost per sample amounts only to a matter of pence.

In attempting to reduce costs it is also worthwhile to take a fresh look at established procedures. Combustion is an almost universal first step in the preparation of samples for radiocarbon dating. Traditionally this has been carried out by various modifications of the method used for elemental analysis of organic materials—the tube furnace. This method is time-consuming and the equipment requires constant attention for periods of 1 to 2 h. Some 10 years ago, the British Museum Research Laboratory looked into the possibility of adapting for radiocarbon dating another established technique of combustion used for the measurement of the calorific value of fuels, that of combustion in oxygen at high pressure in a closed vessel. Preliminary experiments showed promise but final development had to wait until more resources became available. The technique has now been fully developed into a semi-automatic operation in which combustion is almost instantaneous and the human intervention required amounts to only a few minutes for each sample (Barker, Burleigh & Meeks 1969).

These various improvements lead to an increase in output with a corresponding increase in the amount of calculation required to process the data from the liquid scintillation spectrometer. Many laboratories have turned to the computer to displace staff from this type of task to more productive work. Experience at the British Museum indicates that this is very well worthwhile. We have had written for us (A. J. Barker, personal communication, 1969) a very comprehensive Algol programme which replaces almost one man-day per week of calculation and checking of results by about a minute of time on the Atlas computer.

None of these improvements is spectacular in itself, but taken together they have made a substantial contribution to increased productivity of one laboratory to the extent that the output of dates has been more than doubled with no increase in staff. Can one look forward to any further economies? We are looking into the possibility of further improvements in sample preparation. For example, is it worthwhile to redesign the equipment more on the lines of a small-scale chemical plant, perhaps under automatic control. This might well be so if one were operating on a large enough scale. This brings me to a final point on costs—their relationship to the scale of operations. In general, the larger the scale the lower the costs. If one is restricted to samples containing no more than the equivalent of 3 g of carbon, a single liquid

scintillation spectrometer can deal with at least 200 average archaeological samples in a year. If, on the other hand, the sample size can be doubled to 6 g of carbon, the same instrument could handle twice as many samples per year with no reduction in accuracy. The bottleneck with this technique is clearly not set by the instrument nor the samples since the majority of them are big enough to yield 6 g of carbon quite comfortably, and the main impediment now to a large increase in output is the difficulty of recruiting sufficient staff to keep the instrument fed with material.

SUMMARY AND CONCLUSION

To sum up this short review; first, as to the accuracy of radiocarbon dates, the many and complex factors involved make it relatively easy to arrive at erroneous conclusions through incautious comparisons of published dates. Correct manipulation of the standard deviation may not be enough, in itself, to prevent wrong conclusions being reached since the published error term cannot take into account all the factors which influence the accuracy of the date. The existence of discrepancies between radiocarbon and calendar dates does not invalidate the method, although these discrepancies do impose some restrictions on the accuracy of the method in certain regions of time. In the main, however, they do no more than make the application of the method more complex and serve to emphasize the need for closer collaboration between the archaeologist and the scientist in the dating laboratory. Secondly, the liquid scintillation technique provides a means of increasing the output of dates at reduced cost compared with the proportional gas counting technique, with no reduction in the standards of accuracy and a considerable increase in one's confidence in the results. One can expect that facilities for dating will improve throughout the world as it comes into more general use. Certainly in this country the facilities for archaeological dating are no longer limited by purely technical considerations. In fact the only obstacle to a further large increase in output lies in the difficulty of obtaining sufficient staff to operate to full capacity the equipment already in use.

REFERENCES (Barker)

Arnold, J. R. 1954 *Science, N.Y.* **119**, 155.
Barker, H. 1953 *Nature, Lond.* **172**, 631.
Barker, H., Burleigh, R. J. F. & Meeks, N. 1969 *Nature, Lond.* **221**, 49–50.
Barker, H. & Mackey, C. J. 1961 *Radiocarbon* **3**, 39.
Craig, H. 1953 *Geochim. Cosmoch. Acta* **3**, 53.
Damon, P. E., Long, A. & Grey, D. C. 1966 *J. geophys. Res.* **71**, 1055–1063.
Delaney, C. F. G. & McAuley, I. R. 1959 *Sci. Proc. R. Dublin Soc.* A **1**, 1.
Godwin, H. 1962 *Nature, Lond.* **195**, 984.
Libby, W. F. 1949 *Radiocarbon dating* (1st ed.) University of Chicago Press.
Munnich, K. O. 1957 *Science, N.Y.* **126**, 194.
Noakes, J. E., Kim, S. M. & Stipp J. J. 1965 *Proc. 6th Int. Conf. Radiocarbon and Tritium Dating* p. 68.
Olson, E. A. & Broecker, W. S. 1958 *Trans. N.Y. Acad. Sci.* Series II, **20**, 593.
Ralph, E. K. & Michael, H. N. 1967 *Archaeometry* **10**, 3–11.
Ralph, E. K. & Stuckenrath, R. jun. 1960 *Nature, Lond.* **188**, 185–187.
Stuiver, M. & Suess, H. E. 1966 *Radiocarbon* **8**, 534–540.
Suess, H. E. 1965 *J. geophys. Res.* **70**, 5937–5951.
Suess, H. E. 1968 *Meteorological monographs* **8**, 146–150.
Vries, H. de, 1958 *Nederlandse Akad. Wetensch. Proc.*, ser. B, **61**, no. 2, p. 1–9.
Willis, E. H., Tauber, H. & Munnich, K. O. 1960 *Am. J. Sci. Rad. Suppl.* **2**, 1–4.

APPENDIX

TABLE 1

| BM-280 | El Lahun. Reeds. | Uncorrected for isotopic fractionation | 3330 ± 63 |
| BM-280 | El Lahun. Reeds. | Corrected for isotopic fractionation ($\delta^{13}C = -11.1 \pm 1\%_0$) | 3550 ± 65 |

TABLE 2

| BM-17 | Hod Hill. Charcoal. | | 1570 ± 150 |
| BM-47 | Hod Hill. Charcoal. | After separation of rootlets | 2410 ± 150 |

TABLE 3

Antler from submerged forest. West Hartlepool

BM-81	Charred outer layer	8680 ± 180
BM-80	Intermediate zone	8700 ± 180
BM-90	Spongy central zone	8100 ± 180

Ur Series, Royal Graves Period

BM-64	Skeleton of Mes Kalam Shar	3920 ± 150
BM-70	Burnt bone from a clay coffin	4030 ± 150
BM-76	Skeleton of Queen Shub-ad	3990 ± 150

Grimes Graves

| BM-87 | Charcoal, Pit 15 | 4270 ± 150 |
| BM-88 | Antler, Pit 15 | 4050 ± 150 |

South Street, Avebury, Neolithic Long Barrow

BM-356	Charcoal	4760 ± 130
BM-357	Ox vertebrae	4700 ± 135
BM-358	Red Deer antler	4620 ± 140