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PRECISE ^{14}C MEASUREMENT BY LIQUID SCINTILLATION COUNTING

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INTRODUCTION

Radiocarbon dating involves a comparison of the count rate of sample carbon with that of modern reference standard material. To calculate a date the ratio Z must be determined where

$$Z = \frac{N_s - N_b}{N_m - N_b} \tag{1}$$

in which N_s = gross sample count rate (cpm),
N_m = gross reference standard count rate (cpm) determined with National Bureau of Standards oxalic acid, 95 percent of the specific activity of which is taken to be that of a sample aged AD 1950,
N_b = background count rate (cpm).

As the sample, reference standard, and background are prepared and counted in the same way, it is generally assumed that any inaccuracies in experimental technique will be the same for each. For this reason radiocarbon dates are usually quoted with a precision (standard deviation, SD) based on the statistics of counting alone and makes no allowance for errors associated with technique apart from sample dilution and isotopic enrichment. However, in practice, sample, reference standard, and background are not counted in identical fashion, as the precision of a date is improved by accumulating counts from reference standard and background over a prolonged period. As a result, sample, reference standard, and background may be counted on different occasions, and there is a possibility that different errors may arise in each with a resulting loss of accuracy. It should be possible to eliminate this difficulty if *constant* preparatory and counting conditions can be provided by investigating (and correcting for) all foreseeable sources of error. This paper describes such an investigation, the object being to achieve an overall precision on a radiocarbon date of about ±20 yrs in order to make a detailed calibration of the radiocarbon time scale (Pearson and others, 1977).

As the age of sample carbon is given by 8033 $\log_e \frac{Z}{0.95}$ (Callow, Baker, and Hassall, 1965) this target requires a precision of about ±0.25

percent of Z. It was desired to develop a system capable of measuring two samples a week to this precision, assuming the material to have an age equal to one half-life. Sample size was not a limiting factor.

The procedure adopted was to convert sample carbon to benzene according to the method of Barker, Burleigh, and Meeks (1969), but scaled up to produce at least 16 ml benzene per sample, and then assess the ^{14}C content of the benzene in a liquid scintillation spectrometer. A preliminary outline account of the procedure has appeared elsewhere (Pearson and others, 1977).

EVALUATION OF ERRORS AND REQUIREMENTS OF THE COUNTING SYSTEM

The errors encountered in a liquid scintillation dating system fall into three distinct groups. There are, first, the errors associated with the statistics of counting; second, those associated with the uncertainty remaining after corrections have been made to improve the accuracy of measurement; and third, those consequent on the uncertainty surrounding the reproducibility of external source channels ratio (p 10) and the assumption that vial efficiency and background are constant (p 17). The last two groups of errors will be considered together and termed correction errors.

If these correction errors are assumed to be independent of each other and specific to sample, reference standard, and background respectively, each count rate will have to be corrected in turn to give the count rate appropriate to the standard conditions. Errors associated with the corrections made to the components of N_s, N_m, and N_b will each contribute to the total error in the ratio Z. To determine how much error can be allowed in each individual component and so assess what will be required of the counting system, it is necessary first to consider the way in which errors will be propagated through the components.

The general equation for the propagation of errors in a function $X = f(a, b, \ldots n)$ where a, b . . .n are independent variables is

$$\mathrm{Var}(X) = \mathrm{Var}(a)\left(\frac{df}{da}\right)^2 + \mathrm{Var}(b)\left(\frac{df}{db}\right)^2 + \ldots \mathrm{Var}(n)\left(\frac{df}{dn}\right)^2 \tag{2}$$

Terms beyond the first differential are considered insignificant as they are unlikely to be more than about 5 percent of the first differentials in magnitude. There may be significant effects due to covariance between sample, standard, and background, but calculation suggests that the likely error (to be propagated along with other errors) is equivalent at most to ±3 yrs, and, for simplicity, this source of error has been ignored.

From (1) and (2) the variances due to the three components are:

$$\mathrm{Var}(Z) = \mathrm{Var}(N_s)\left(\frac{dZ}{dN_s}\right)^2 + \mathrm{Var}(N_m)\left(\frac{dZ}{dN_m}\right)^2 + \mathrm{Var}(N_b)\left(\frac{dZ}{dN_b}\right)^2 \tag{3}$$

and substituting from (1) following differentiation

$$\mathrm{Var}(Z) = \mathrm{Var}(N_s)\left(\frac{1}{N_m - N_b}\right)^2 + \mathrm{Var}(N_m)\left(\frac{N_s - N_b}{(N_m - N_b)^2}\right)^2$$
$$+ \mathrm{Var}(N_b)\left(\frac{N_m - N_s}{(N_m - N_b)^2}\right)^2$$

Dividing through by $Z^2 = \left(\frac{N_s - N_b}{N_m - N_b}\right)^2$ gives $\frac{\mathrm{Var}(Z)}{Z^2} = \frac{\mathrm{Var}(N_s)}{(N_s - N_b)^2}$

$$+ \frac{\mathrm{Var}(N_m)}{(N_m - N_b)^2} + \mathrm{Var}(N_b)\left(\frac{N_m - N_s}{(N_s - N_b)(N_m - N_b)}\right)^2 \qquad (4)$$

The maximum permissible error in Z is ±0.25 percent. Hence

$$\frac{\mathrm{Var}(Z)}{Z^2} = \left(\frac{0.25}{100}\right)^2 = \frac{\mathrm{Var}(N_s)}{(N_s - N_b)^2} + \frac{\mathrm{Var}(N_m)}{(N_m - N_b)^2}$$
$$+ \mathrm{Var}(N_b)\left(\frac{N_m - N_s}{(N_s - N_b)(N_m - N_b)}\right)^2 \quad . . . (5)$$

From this equation it is possible to evaluate the relative significance of the errors in the components of N_s, N_m, and N_b. In order to obtain optimum precision on a radiocarbon date in a fixed period of time, the conditions of operation should be such as to give identical fractional errors for each component. However, in the present investigation, a major portion of the error allowance was awarded for sample measurement so as to reduce counting time to a minimum and allow two samples to be measured each week. Although the correction errors on the background all involve the linear addition or subtraction of counts, the correction errors on the sample and reference standard are of two types: the fractional or percentage errors which result from changes in efficiency and errors of the additive type. As it is not possible, at this stage, to evaluate these combinations of correction errors, the variances of each component were assumed to be equal, that is,

$$\mathrm{Var}(N_s) = \mathrm{Var}(N_m) = \mathrm{Var}(N_b) = x^2$$

This assumption increases the error allowance on the sample because the count rate of the sample will generally be less than that of the reference standard. The error allowance on the reference standard is correspondingly reduced, but the standard could still be measured to a high precision as counts could be accumulated over a period of months. To simplify the equations let $N_s = 0.5\ N_m = 1$ and substitute into (5).

Then

$$\frac{\mathrm{Var}(Z)}{Z^2} = \left(\frac{0.25}{100}\right)^2 = \frac{x^2}{1} + \frac{x^2}{4} + \frac{x^2}{4} \text{ when } N_b = 0 \quad . . \qquad (6)$$

$$\frac{\mathrm{Var}(Z)}{Z^2} = \left(\frac{0.25}{100}\right)^2 = \frac{x^2}{0.83} + \frac{x^2}{3.64} + \frac{x^2}{3.01} \text{ when } N_b = 0.1(N_s - N_b) \qquad (7)$$

$$\frac{\mathrm{Var}(Z)}{Z^2} = \left(\frac{0.25}{100}\right)^2 = \frac{x^2}{0.69} + \frac{x^2}{3.36} + \frac{x^2}{2.33} \text{ when } N_b = 0.2(N_s - N_b) \qquad (8)$$

Consider eq (6) above. The three terms on the right refer to the fractional variances in N_s, N_m, and N_b respectively (5), and it is clear that the fractional variance of the sample is four times that of the standard or background. This gives a basis, albeit approximate, on which to work. The fractional variance of N_s is 0.667 of the total error, that is,

$$\frac{\mathrm{Var}(N_s)}{(N_s - N_b)^2} = 0.667 \left(\frac{\mathrm{Var}(Z)}{Z^2}\right) = 0.667 \left(\frac{0.25}{100}\right)^2 = \left(\frac{0.204}{100}\right)^2$$

The corresponding fractional variance for N_m is

$$\frac{\mathrm{Var}(N_m)}{(N_m - N_b)^2} = 0.167 \left(\frac{\mathrm{Var}(Z)}{Z^2}\right) = 0.167 \left(\frac{0.25}{100}\right)^2 = \left(\frac{0.102}{100}\right)^2$$

and for N_b

$$\mathrm{Var}(N_b)\left(\frac{(N_s - N_m)}{(N_m - N_b)\,(N_s - N_b)}\right)^2 = 0.167\left(\frac{\mathrm{Var}(Z)}{Z^2}\right) = 0.167 \left(\frac{0.25}{100}\right)^2$$

$$= \left(\frac{0.102}{100}\right)^2$$

Similar evaluations of eqs (7) and (8) allow the effect of background level on the fractional errors on the components due to N_s, N_m, and N_b to be determined:

Background level	$\frac{SD\,(N_s)}{N_s - N_b}$	$\frac{SD\,(N_m)}{N_m - N_b}$	$\frac{SD\,(N_b)\,(N_m - N_s)}{(N_s - N_b)\,(N_m - N_b)}$
$N_b = 0$	0.204 percent	0.102 percent	0.102 percent
$N_b = 0.1(N_s - N_b)$	0.204 percent	0.098 percent	0.107 percent
$N_b = 0.2(N_s - N_b)$	0.204 percent	0.093 percent	0.111 percent

It can be seen that changes in the background component from 0 to 20 percent of the net sample count rate have little effect. A background of 15 percent of the net sample count rate was taken as a realistic aim, that is,

$$N_b = 0.15\,(N_s - N_b) \qquad (9)$$

The fractional errors are then 0.204, 0.095, and 0.109 percent, respectively.

Since these error allowances include a combination of both correction errors and counting errors, a further breakdown of the error allowance is necessary. Twelve factors likely to give rise to correction errors in the final result in a liquid scintillation counting system were envisaged. (As the samples were not to be diluted with inactive benzene no allowance has been made for dilution errors.)

Isotopic enrichment
Background variation with barometric pressure
Reproducibility of external source channels ratio
Loss of sample benzene
Variation of efficiency with weight of vial contents

Variation of background with weight of vial contents
Contamination with ^{3}H
Contamination with ^{222}Rn
Variation of efficiency with "purity" (p 10)
Variation of background with "purity" (p 11)
Variation of efficiency between vials
Variation of background between vials

Since the ultimate accuracy of a ^{14}C measurement is dictated by the limitations of the counter used, it was intended to select an instrument capable of a stability that would allow correction to standardized conditions to within ±0.025 percent for efficiency and ±0.025 percent of net sample count rate for background. The accuracy of purely physical measurements can often be improved by repetition, and it was estimated that an accuracy of ±0.01 percent could be achieved in this way for measurement of weight, atmospheric pressure, and isotopic enrichment. It was hoped to achieve the same level of accuracy for all the individual correction factors but to take account of additional errors (such as those due to the human element and those involved in determining the magnitude of factors for which corrections have to be applied) the allowable precision on each correction was raised to ±0.025 percent in the case of fractional errors or ±0.025 percent of net sample cpm for errors involving the linear accumulation of counts. The total cumulative error due to the 12 factors listed above gives a precision (calculated from the root mean square value of individual errors) equivalent to ±0.087 percent of net sample count rate. However, only half the corrections are of the fractional type, the remainder being additive, and, since these are equivalent to ±0.0125 percent of net *standard* count rate, the cumulative correction errors on the reference standard is only 0.068 percent of net reference standard count rate. The correction errors involved in standardizing background measurement are all of the additive type and give a cumulative error equivalent to 0.061 percent of net sample count rate. Knowing these correction errors, it is now possible to calculate the residual error allowance that can be allocated to N_s (0.185 percent) and N_m (0.066 percent). From these figures, the requirements of the counting system can soon be deduced.

Consider first the sample component. It is required that

$$\frac{SD\ (N_s)}{N_s - N_b} = 0.185 \text{ percent}$$

Substituting from (9), it can be shown that

$$\frac{SD\ (N_s)}{N_s} = 0.87 \times 0.185 \text{ percent} = 0.161 \text{ percent}$$

Such a fractional error requires that about 386,000 counts be observed. If the ^{14}C efficiency is 70 percent, a half-life sample will give a count rate of about 5 cpm/g carbon or 5.75 cpm/g including background. Allowing 2.75 days to count each sample means that a total of 23,000 counts will be accumulated per g carbon. To achieve the desired precision 16.8 g carbon must therefore be measured. This will result in a net count rate of 84 cpm and a background of about 12.6 cpm.

The remaining error on the reference standard component $\frac{SD\ (N_m)}{N_m - N_b}$ is 0.066 percent so that

$$\frac{SD\ (N_m)}{N_m} = 0.93 \times 0.066 \text{ percent} = 0.061 \text{ percent}$$

To achieve this precision the reference standard must be counted for approx 3×10^6 counts. As the count rate N_m will be about 181 cpm, this will take 16,600 min, that is, 1 day a week for about 11 weeks.

The overall fractional error allowance for the background is 0.109 percent. Substituting for N_s, N_m, and N_b into the third term of eq (5) yields

$$\frac{SD\ (N_b) \times 97}{84 \times 181} = 0.109 \text{ percent}$$

Hence $SD\ (N_b) = 0.174$ cpm.

Now the correction error on the background was shown above to be equivalent to 0.061 percent of net sample count rate, that is, 0.051 cpm. The remaining error that can be allowed for background counting is then 0.166 cpm. To count a background of 12.6 cpm to a precision of ±0.166 cpm requires about 6000 counts, that is, about 8 hours counting time.

THE COUNTER

After a survey of the instruments then available, using the above specification as a guide, a Philip's Liquid Scintillation Analyzer, type PW 4510 was purchased in 1970 and modified as follows: A matched pair of photo-multiplier tubes was selected for low background in the ^{14}C energy range, and the light guides were altered to give the highest possible figure of merit for ^{14}C. The counter was installed in a single story building and surrounded on three sides with a concrete shield with 30-cm-thick walls and 75cm overhead. The background count rate was then 9.3 cpm. The long-term temperature control of the instrument was improved by the addition of automatic defrosting, and a second circulatory fan was installed to minimize the temperature gradient within the counter cabinet.

The basic assembly had 21 independently-programmable trays each containing up to 20 samples, stored in the temperature-controlled cabinet and cycled automatically. The samples were measured by coincidence counting (resolving time 10 ns), and after coincident pulse summation, the spectrum of voltage pulse height was analyzed in three separate and independent channels set to monitor, respectively, ^{3}H (a possible and variable contaminant in the water supply used in the synthesis of benzene from sample carbon), ^{14}C, and, ^{222}Rn, which was a major source of contamination in both the water supply and the lithium metal used in the synthesis of benzene (Pearson, unpub.). External monitoring facilities were provided by a 7 μCi ^{133}Ba collimated source using two additional, independent channels.

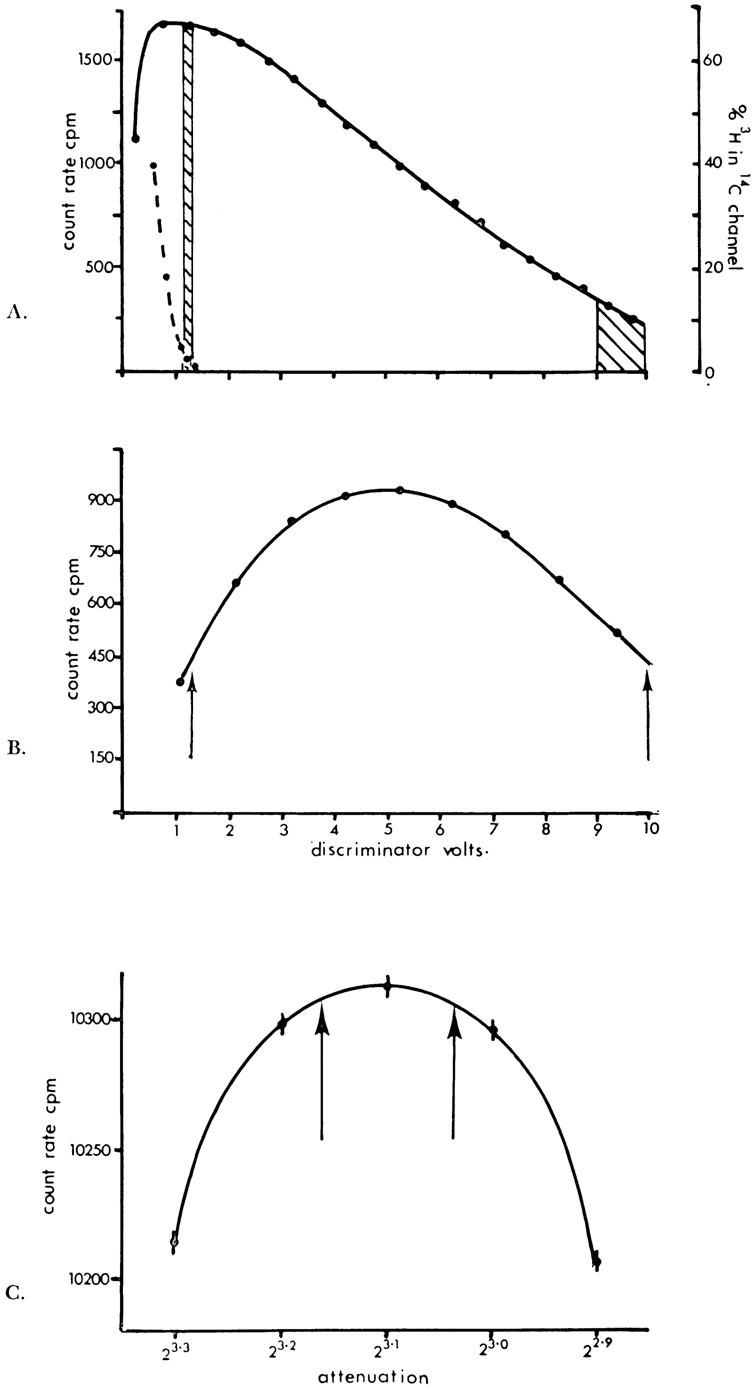
Particular care was taken to set up the instrument in such a way as to elicit from it the best performance. Since ^{3}H was the isotope with the lowest energy to be measured and therefore required the highest overall gain, this channel was used to determine the operating voltage of the photomultipliers, the voltage being increased until the highest count rate was obtained for a ^{3}H source at a low attenuation setting and with a dynamic range of 25:1.

Each photomultiplier tube was then set to give the maximum pulse height by adjusting the focusing grid voltage and then the acceleration voltage. The high voltage supply to each tube was next adjusted to balance the tubes so that each gave a similar pulse height spectrum when observing the same counting vial. Finally, the ^{3}H channel attenuation was readjusted to give the maximum count rate.

To set the ^{14}C channel so as to exclude any major contribution from ^{3}H but yet operate at balance point, the discriminators were initially fixed to give a dynamic range of about 7:1. The amplifier gain was then increased to give the maximal count rate within this dynamic range. To ensure that corrections could be made within the designated limits for any counts recorded in the ^{14}C channel from contaminant ^{3}H, the discriminators on the ^{3}H channel were altered to reduce the efficiency (to about 30 percent) with a dynamic range of only 12:1. (Approx 8 percent of the ^{14}C counts observed in the ^{14}C channel then contributed to the ^{3}H channel.) To keep the error caused by any ^{3}H contribution to the ^{14}C channel below ±0.025 percent of the net sample count rate of ^{14}C, that is, below ±0.02 cpm, this value was set as the SD of the error in the assessment of ^{3}H contributions to the ^{14}C channel. It was calculated that ^{3}H could be determined under all conditions to better than ±1 cpm, thus allowing a maximum of 2 percent of the net ^{3}H count rate to contribute to the ^{14}C channel. The lower level discriminator in the ^{14}C channel was set to 1.30 volts which in fact gave a contribution of about 1 percent (fig. 1A), allowing for a possible increase in contribution if there were a rise in overall gain. The limit of detection for ^{3}H in the ^{3}H channel was 0.04 cpm with ^{14}C-free benzene.

Because at this stage, the gain of the ^{14}C channel had been fixed and the lower level discriminator had been set to reduce the ^{3}H contribution, it was no longer possible to use the conventional method (Dyer, 1974) to reestablish a balance point in the ^{14}C channel. The balance point is the most stable point for counting operations, since the net loss of counts from the channel due to any variation in overall gain is minimal. As gain is a percentage function, any change in gain increases each part of the pulse height spectrum by the same proportion. The effect of such a change can be represented by an equal percentage change in the upper and lower level discriminator voltages defining the channel. The counts in the area bounded by the movement of the upper discriminator voltage are then

FIGURE 1


A.
count rate cpm
1500
1000
500
% ³H in ¹⁴C channel
60
40
20
0
B.
count rate cpm
900
750
600
450
300
150
1
2
3
4
5
6
7
8
9
10
discriminator volts
C.
count rate cpm
10300
10250
10200
2^3·3
2^3·2
2^3·1
2^3·0
2^2·9
attenuation

equal to the counts in the area defined by the movement of the lower discriminator voltage (fig. 1A).

To simulate the effect of a change in gain, a scan of the ^{14}C voltage pulse height spectrum was therefore made by varying the lower level discriminator voltage and setting the channel width at 10 percent of this voltage. Figure 1B shows an almost symmetrical pulse height distribution; for balance point operation the upper and lower level discriminator settings must intersect the curve at an identical count rate on either side of the peak. The lower level discriminator had already been set at 1.30 volts; to intersect the curve at the same count rate the upper level was now fixed at 10.0 volts. By this means balance point could be set accurately since the discriminator levels could be adjusted to within 1 percent, while attenuation settings, which are normally used to find the balance point, could only be set to the nearest incremental position, giving a possible deviation of 3.5 percent.

With these settings the dynamic range was 7.7:1, the efficiency (E) for ^{14}C was about 73 percent, and the net count rate for the reference standard was 122.9 cpm. The figure of merit E^2/N_b was 574, and $(N_m - N_b)^2/N_b$ was 1624.

The ^{222}Rn channel was set immediately above the end point energy for ^{14}C with maximal channel width.

PULSE HEIGHT VARIATION

The photomultiplier tubes were sensitive to temperature, but they were housed in a refrigerated cabinet set at 10 ± 1°C; they would, however, not experience the whole of the fluctuation within these limits because the variations were short term, and there was a shield of high thermal capacity around the photomultiplier tubes. No significant change in gain was observed between laboratory temperatures of 9° and 25°C.

The relative voltage pulse heights are the voltage pulse heights obtained per unit energy absorbed on different occasions or under different conditions. Relative voltage pulse height may be affected by the presence

←— A. Pulse height spectrum for ^{14}C and ^{3}H in the ^{14}C channel. Counts were determined with a 0.5 volt channel width (—●—). The shaded trapezoidal areas are bounded by the movement of discriminator voltage levels required for a 10 percent decrease in gain; these areas are approximately equal. Contribution made by ^{3}H to the ^{14}C channel (—●—). Sources were flame-sealed vials containing ^{14}C and ^{3}H-labelled benzene, respectively, each giving the same relative voltage pulse height.

B. Pulse height spectrum for ^{14}C in which count rates were determined as a function of the lower discriminator voltage, channel widths being equal to 10 percent of this voltage for each measurement. A and B are the two discriminator levels intersecting the count rate curve at identical count rates on either side of the peak (see text).

C. Pulse height spectrum for ^{14}C around the balance point, determined by change of attenuation with fixed discriminator settings. The graph corresponds to the central region of (B). The points show count rates at each successive attenuation setting. A curve drawn by eye through these points would not be sufficiently accurate to allow corrections to the required precision, and the curve has therefore been calculated from the slight differences in area between pairs of trapezia like those shown in (A); for each consecutive unit change of gain setting, the count rate was found to fall according to the series 1, 3, 6, 10, 15, . . . calculated from the slight differences in area between pairs of trapezia 6, 10, 15, . . . The balance point is at the peak of the curve, and the arrows indicate a change in gain of ±4.5 percent from this point; if no correction were made, there would be a drop of 0.034 percent in counting efficiency at these limits.

of solutes which may quench or increase pulse height. Mass spectrometric analysis of samples of benzene synthesized from cellulose failed to reveal any significant traces of toluene or other foreign compounds. Furthermore, scintillation grade benzene (which was used for background measurements) gave just the same relative voltage pulse height spectrum as synthesized benzene and, therefore, contained no significant impurities; however, this was not true of all samples of Analar benzene. The concentration of oxygen (which has a quenching effect, Birks, 1970) in samples of benzene, will depend on the ambient temperature and pressure at the time the vial is filled, but as the vials were hermetically sealed any differences in concentration would persist even though the samples were all finally measured at the same temperature.

The external ^{133}Ba source was used to monitor the purity of each sample of benzene by examining its pulse height spectrum on each occasion that it was counted. The Compton electron continuum produced in the vial from the ^{133}Ba γ-radiation corresponds roughly to the ^{14}C β-spectrum and is therefore subject to the same factors that influence pulse height variation. The pulse height spectrum from the ^{133}Ba was split into two portions, each measured in a separate channel, in such a way that the ratio of counts for lower to higher energies was about 2 to 1. Any change in overall gain would affect the relative voltage pulse heights, moving pulses from one channel to the other, thus changing the ratio of the count rates for the two channels. The magnitude of this change was determined in experiments using ^{14}C benzene quenched with varying amounts of methanol. Over the range of gain changes accepted, the ratio increased by 1 percent for a 1.5 percent decrease in relative voltage pulse height. The ratio was also used on a long-term basis to monitor variations of relative voltage pulse height due to changes in overall gain irrespective of sample purity. The term "purity" is used to refer to any deviation in the ratio, whether due to the presence of some impurity in the benzene or to other factors affecting overall gain.

At least 40 external source channels ratio determinations were accumulated for each sample of benzene counted, the mean value being used as an index of variation in pulse height. The SD attached to this mean (± 0.5 percent) was that of a single measurement, as there was no certainty that repeated measurements would fall within a normal distribution.

Balance point operation reduces the effect that small changes in relative voltage pulse height may have on efficiency, but it does not provide a *constant* counting efficiency. Maximum efficiency can only be obtained for a particular pulse height spectrum within a defined channel at one particular gain setting, the balance point position (fig. 1C). Since any changes in relative voltage pulse height cause a deviation from this point and reduce counting efficiency, it was necessary to make the appropriate corrections, so simulating a constant efficiency. The balance point position was initially set using benzene of average purity, selected from among samples of scintillation grade benzene and synthesized benzene. This sample of average purity yielded an external source channels ratio of 1.95, and in subsequent work, all ^{14}C benzene count rates were corrected to this value of channels ratio.

It was assumed in the work of Pearson and others (1977) that, within limits, efficiency was proportional to the external source channels ratio. To achieve the required precision, the maximum permissible deviation of the external source channels ratio was limited to ±3 percent, that is, ±4.5 percent deviation in relative voltage pulse height, when efficiency was reduced by 0.034 percent of net count rate. Correction factors were calculated at 1 percent deviation intervals giving about 0.01 percent change in efficiency for each percent change in channels ratio. Because the external source channels ratio was measured to ±0.05 percent, the SD error on this correction was 0.005 percent of net cpm. (The assumption that efficiency is proportional to the channels ratio is only an approximation, as it can be seen from fig. 1A that any change in gain results in a net loss of counts from the channel equivalent to the difference in area between the pairs of trapezia. Fig. 1C is a curve that takes into account these differences in area; it would provide a more accurate basis for assessing the correction factors.)

Since background measurements have a quite different energy spectrum to that derived from ^{14}C, it was necessary to determine the effect of variation in pulse height on background. Vials filled with the standard quantity of ^{14}C-free benzene were measured at intervals over a 100-fold range of attenuation, each measurement being made to better than ±1 percent. Over the relatively narrow range of pulse heights accepted, each 1 percent increase in external source channels ratio caused a fall of 0.041 cpm in background. When this relationship was used to calculate the background corresponding to a channels ratio of 1.95 ± 0.05 percent there remained an error in the correction of about ±0.02 cpm; because it was uncertain whether external source channels ratio measurements would fall into a normal distribution, it was decided to use 2 SD limits, that is, ±0.041 cpm (equivalent to ±0.070 percent of net sample cpm).

THE VIALS

As plastic vials proved unsatisfactory for counting benzene, vials (20 ml) of low-potassium glass with screw-on plastic caps containing a cork and aluminum seal were chosen. Following preliminary trials with 500 such vials which yielded a large spread of background measurements, a group of twenty vials within a weight range of 14.2 to 14.3g was selected. The cork and aluminum seals were found to allow an excessive loss of benzene—more than 5mg per day. New seals were therefore made with a disc of viton rubber (1.5mm thick) giving compression and high restitution, followed by a PTFE disc (0.4mm thick), providing a low friction backing to reduce the possibility of creasing in the final disc, which was made of high purity tin (0.1mm thick), chosen for its properties of compression and reflection. With this type of seal, losses were reduced to 1mg per day. As the physical shape of the vials above a volume of 18ml varied from vial to vial, the internal scatter of photons and the solid-angle geometry of light emission were standardized by spraying the vials above 18 ml with matt white paint, covered in turn with black paint to reduce optical feedback from one photomultiplier to the other.

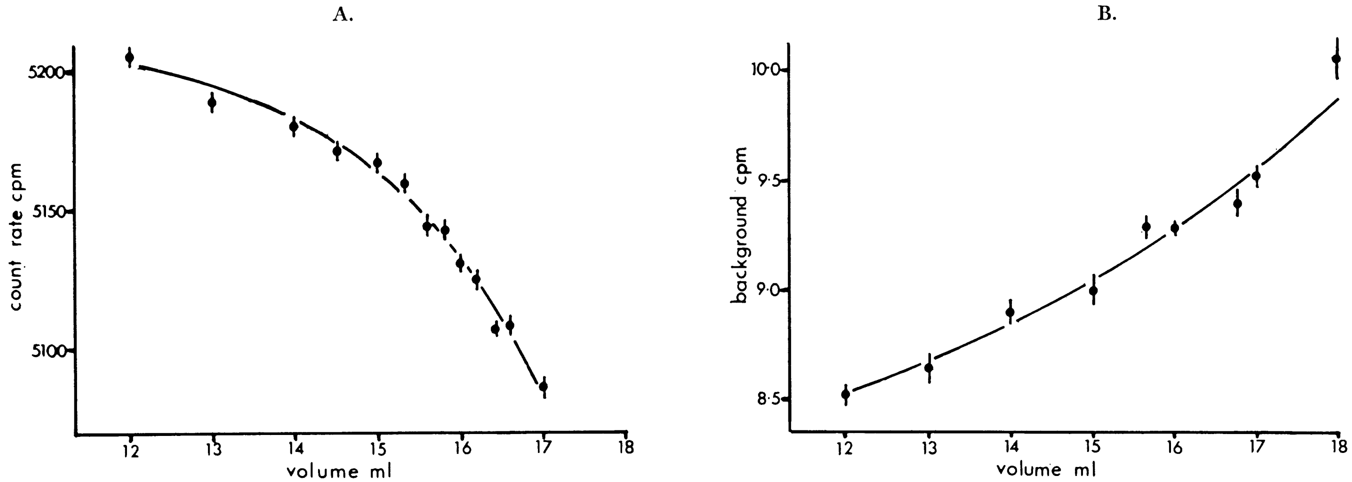
To ensure that each vial was filled with the same amount of sample and scintillant (so reproducing identical geometry, energy-photon conversion, and background counts), filling was monitored by weight rather than volume. The scintillant was a solution of butyl-PBD and PBBO in scintillation grade toluene, giving final concentrations in the vial of 10g/l and 0.6g/l, respectively (Dyer, 1974).

The vials to be filled were first cleaned with Decon 90, dried, and weighed with and without the final sealing cap. Slightly less than 15ml of sample benzene was then pipetted into the vial. A specially made filling cap (similar to the sealing cap but with a hole drilled through the shell) was weighed and screwed on to seal the vial. The additional sample benzene required to make up a total of 13.1325g was added by means of a micrometer-controlled pipette through a very fine hypodermic needle, a second needle being inserted into the vial for pressure equilibration; the appropriate number of drops was added, and the final weight checked. The addition of 1.1340g of scintillant was achieved in the same manner. Finally the filling cap was replaced with the permanent sealing cap, care being exercised to ensure that no more than 3mg of the mixture was lost by evaporation at this stage. The weight was finally checked before the vial was loaded into the counter, so that losses of sample benzene before counting could be calculated. After the required period of counting, the vial was weighed again.

It was discovered that the weight of a plastic vial cap can itself change by more than 5mg in a matter of minutes. The extent of this change in weight depends on humidity, temperature, and time, and it may be as large as 40mg over a period of 14 days. A correction was made for such changes in weight, determined by experiments with empty vials conducted under the routine conditions. Weight loss could then be estimated to ±10mg, equivalent to an error of ±0.070 percent, a figure representing the maximum error rather than a SD error. (More recently caps made of low-lead aluminum alloy have been used as they show no change in weight with temperature or humidity and bring the accuracy of weight measurement to ±3mg, that is, ±0.021 percent.)

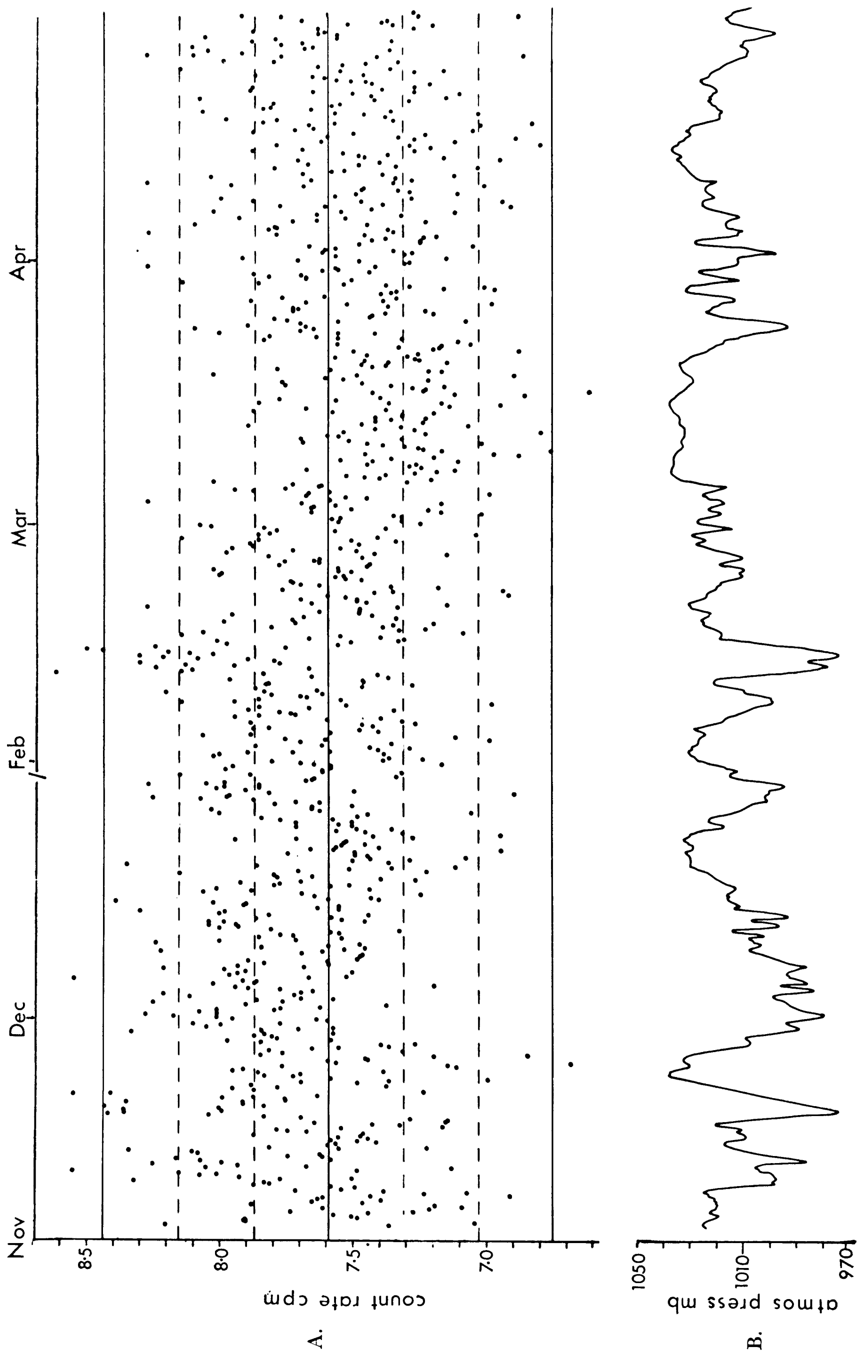
Although the vial caps gave a good seal, over the long periods needed to count samples of low specific activity, appreciable losses owing to evaporation sometimes occurred—up to 50mg over 2 to 3 months. Such weight losses affect efficiency as a result of small changes in the solid-angle geometry presented by the sample to the photomultiplier. Around the standard weight of 14.2666g benzene plus scintillant, the count rate rises by 0.001 percent per mg loss in weight (fig. 2A). This relationship was used to calculate the count rate of each sample or reference standard at the standard weight, assuming that the weight losses were linear over the entire counting period. Since the vial weight could only be measured to ±10mg, the maximum error remaining after this correction was estimated to be ±0.01 percent of net cpm.

FIGURE 2



A. Efficiency of counting ^{14}C in relation to volume of sample. A constant quantity of ^{14}C benzene (10 ml, 10^5 dpm) was diluted with successive aliquots of scintillation grade benzene in such a way that the ratio of scintillant to benzene remained constant.

B. Variation of background in relation to volume of scintillation grade benzene, the proportion of scintillant to benzene remaining constant. Efficiency and background were both taken to be linear functions of volume within the range 16 ± 0.1 ml.


Nov
Dec
Feb
Mar
Apr
8·5
8·0
7·5
7·0
count rate cpm
A.
1050
1010
970
atmos press mb
B.

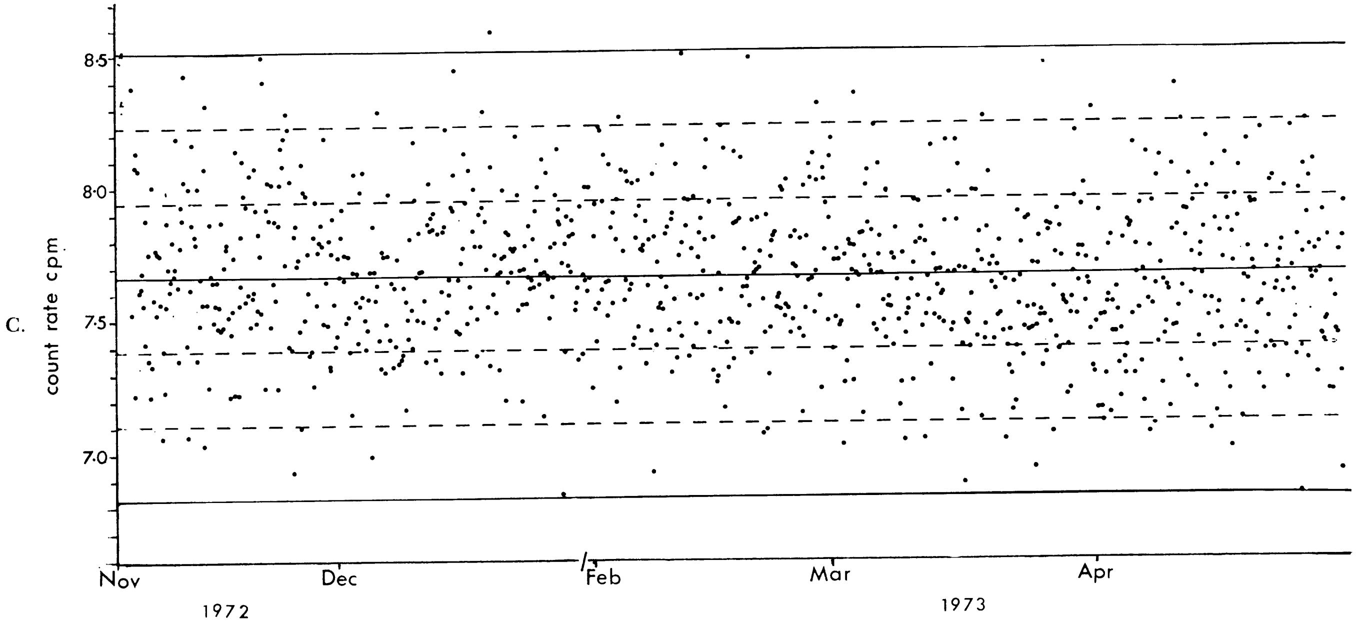


Fig. 3. Background measurements made with a single vial containing ^{14}C-free toluene twice a day over a 6 month period (with an interval of 1 month as shown after the first 2 months). The horizontal lines show mean cpm and 1, 2 and 3 SD limits above and below the mean. (A) Observed values. Note that the mean value for the first 3 months is higher than that in the subsequent period. (B) Corresponding atmospheric pressure chart showing the opposite trend, being higher in the last 3 months. The same inverse relationship is also evident in some of the short-term fluctuations. (C) The same data as in (A), corrected for atmospheric pressure changes. No adjustment was made to the overall gain during the 6-month period nor was there any correction for changes in gain, that is, "purity"; the slow downward drift in count rates indicates a progressive decline in gain.

Background counts were found to fall by 0.00029 cpm per mg loss of weight (fig. 2B), a relationship that was used to calculate background count rates at the standard weight; the error (maximal error) on this correction was ±0.003 cpm, that is, ±0.005 percent of net sample cpm.

A further correction was applied to allow for the loss of sample benzene during the counting period. The overall weight of benzene and scintillant lost during the counting period was known, but only 98.3 percent (w/w) of this weight was due to the loss of benzene (the remainder being due to loss of toluene). The mean weight of benzene present during the counting period was used to calculate the count rate for the standard weight of benzene (13.1325g); the estimated error on this correction was ±0.076 percent of net cpm. As the estimate of the weight error (±10mg) used to derive this correction was a maximum figure, no additional error component was included to allow for the precision within which the differential loss of benzene was determined.

BACKGROUND DETERMINATION: INFLUENCE OF ATMOSPHERIC PRESSURE

The long-term stability of background determination was initially assessed with the two flame-sealed vials containing 15ml of ^{14}C-free toluene and scintillant that were supplied with the counter. The vial backgrounds were each counted for 100 min (to give a precision of about ±3 percent) twice a day. Counting was continued over a 9-month period. Although the count rate was sufficient to ensure a close approximation to a normal distribution, nevertheless, the count rates were found to vary beyond the expected distribution (fig. 3A), only 60.7 percent of the counts falling within one SD of the mean compared to the theoretical 68.3 percent. The deviations from the expected numbers of counts falling within one, between one and two, and beyond two SD were significant at the 1 percent level.

Investigation of periods where a number of points came together outside 2 or 3 SD limits from the mean revealed that barometric pressure was extreme at these times (fig. 3B). There was in fact a significant regression with a coefficient of −0.0120 cpm per mbar increase in pressure. When the background measurements for the 9-month period were corrected to a barometric pressure of 1010 mbar, the counts so obtained fell into a normal distribution (fig. 3C), 68.5 percent of the results then being within one SD from the mean and other percentages in similar agreement with the theoretical values.

This effect of atmospheric pressure was also found to be important under the routine working conditions. Background measurements were accumulated with vials containing 16ml *benzene* and scintillant over a 2-yr period. When the counts recorded were corrected for weight loss, a high degree of correlation was again revealed, with a coefficient of −0.0127 cpm per mbar increase in pressure. This relationship was used to correct each measurement to a standard pressure of 1010mbar. At least 40 pressure readings were taken for each sample determination (and more for standards and backgrounds). It was estimated that the error on the mean atmospheric pressure, including the error inherent in the correlation coefficient, would be ±1 mbar, that is, ±0.013 cpm, which is equivalent to 0.019 percent of net sample cpm.

COUNTING PROCEDURE

The schedule of counting operations is shown in table 1.

The count rate of the high activity ^{3}H and ^{14}C toluene sources were plotted daily to provide quality control charts for their respective channels, as was the external source channels ratio. This information was used to index the long-term drift of the instrument. Toluene was chosen rather than benzene as the relative voltage pulse height per m.e.v. from toluene is greater than that from benezene, so that tolune was not counted at balance point for either ^{3}H or ^{14}C, rendering any changes in overall gain more readily detectable. After about a year, the external source channels ratio (and also the counts from the radioactive toluene sources) showed a change in gain sufficient to cause a 3 percent shift from balance point. The channels ratio was then returned to 1.95 by adjusting the photomultiplier voltages and cleaning the light guides and the end windows of the photomultipliers.

Quality control charts were also kept for the observed count rates in the ^{3}H and ^{14}C channels and the external source channels ratio for all standard and background measurements. The replicate count rates observed in successive counting cycles from each sample were corrected for atmospheric pressure and then submitted to a χ^2 test to detect any unexpected deviation.

Any ^{222}Rn present in a sample would make a significant contribution to both the ^{3}H and ^{14}C channels and for this reason care was taken to remove contaminating radon during sample preparation. The high efficiency of the ^{222}Rn channel enabled any remaining contamination to be recognized and the samples rejected at an early stage.

At the end of the counting period, the mean count rate for a sample or reference standard was first corrected for any change in the background that would have occurred due to deviation from the standard conditions

TABLE 1

Schedule of counting operations

	Counting time allowed in each cycle of 12 h	Period of time in counter
5 samples	100 min each	About 3 weeks
2 reference standards	40 " "	One renewed every 3 months to allow overlap between the two (it was not known whether weight loss from vials would be linear over longer periods).
Background vials	100 "	Normally 3.5 days
Flame-sealed ^{3}H toluene standard	4 "	Continuous: monitors ^{3}H
Flame-sealed ^{14}C toluene standard	4 "	" " ^{14}C
Flame-sealed ^{14}C-free toluene standard	40 "	" " background

of the variable components of background, that is to say atmospheric pressure, "purity", and weight loss. The net count rates were then evaluated by subtracting the current grand mean value of background under standard conditions. Corrections were finally made to sample and reference standard counts for changes in isotopic enrichment and efficiency (due to weight loss, "purity", and loss of sample). In this way, each count rate was brought to standard conditions. The corrected values for reference standard and background for a particular vial were then compared with the values accumulated previously for that vial and used to calculate again grand mean values for standard and background; the values never fell outside the range expected of a normal distribution, indicating that there had been no significant change of efficiency or background with time, and (by inference) that the corrections were accurate.

The individual grand mean values of background and reference standard were determined for each of the 12 individual vials currently in use. No indication of any significant differences in vial efficiency emerged from experiments in which (A) the reference standard was determined to better than 0.1 percent, or (B) a high specific activity ^{14}C source was counted to ±0.029 percent. It was concluded that any change in efficiency between vials lay within these latter limits.

Backgrounds were determined to ±0.3 percent. Although no significant difference in background between vials was detected, the possibility still exists that each vial has its own unique value, and for this reason two SD limits were used in the overall error estimation, that is, ±0.058 cpm equivalent to about 0.01 percent of net sample cpm. Final values for reference standard and background were, therefore, based on the corrected results for all the vials, accumulated over a 2-yr period.

After each count of a sample or reference standard, the vial was cleaned, dried, and filled with scintillation grade benzene to ensure that it gave a background measurement within the distribution already established for that vial.

The corrected count rates were used to calculate the radiocarbon date. To evaluate the precision of this date it is necessary to accumulate the errors remaining after the appropriate corrections have been made to each of the three components N_s, N_m, and N_b. For this purpose, additive errors must first be expressed as a fraction of the respective net cpm. The individual correction errors and counting errors on a sample measurement are propagated as the root mean square of the individual fractional errors. Hence, the fractional error on N_s is given by:

$$\frac{\mathrm{Var}(N_s)}{(N_s - N_b)^2} = (a^2 + b^2 + \ldots + n^2)$$

and

$$\frac{\mathrm{Var}(N_m)}{(N_s - N_b)^2} = (a_1{}^2 + b_1{}^2 + \ldots + n_1{}^2)$$

where a, b, . . . n are individual fractional errors on samples and a_1, b_1 . . . n_1 are errors on the reference standard. The individual count rate errors on the background measurements ($a_2, b_2, \ldots n_2$) are summed in the same way.

$$\mathrm{Var}(N_b) = a_2^2 + b_2^2 + \ldots n_2^2$$

Substituting these values into eq (5)

$$\frac{\mathrm{Var}(Z)}{Z^2} = (a^2 + b^2 + \ldots n^2) + (a_1^2 + b_1^2 + \ldots n_1^2) + (a_2^2 + b_2^2 + \ldots n_2^2)\left(\frac{N_m - N_s}{(N_m - N_b)(N_s - N_b)}\right)^2$$

The error on an age determination is then given by the expression

$$8033 \log_e \left(1 \pm \frac{SD\,(Z)}{0.95\,Z}\right) \text{ yrs}$$

DISCUSSION

It was desired initially to measure the ^{14}C activity of two samples per week each aged about one half-life and to derive a radiocarbon date within an overall precision of ±0.25 percent, that is, approx ±20 yrs. To achieve this precision it was hoped to keep the error on each factor to less than ±0.025 percent of net cpm or (in the case of additive errors) that equivalent to ±0.025 percent of net sample cpm. This target was achieved for all the factors apart from the four discussed below. The correction errors on some of the factors were so low as to allow these four to be slightly greater than ±0.025 percent. Thus the correction error on variation of efficiency with purity was only ±0.005 percent of net cpm, and the variation of background with weight was equivalent to an error of ±0.005 percent of net sample cpm. No ^3H or ^{222}Rn contamination was detected at all (and the limits of detection were so fine as to ensure that no significant error was introduced through failure to monitor contamination actually present).

The four factors with larger correction errors are:

1. variation of background with "purity" (±0.041 cpm, equivalent to an error of ±0.070 percent of net sample cpm);
2. variation of background between vials (±0.058 cpm, equivalent to an error of ±0.01 percent of net sample cpm);
3. correction for loss of sample benzene (±0.076 percent of net cpm); and
4. correction for isotopic enrichment. Individual measurements on the mass spectrometer were made to give a correction to the observed net count rate of ±0.02 percent. However, when analyses were repeated on subsequent occasions, the overall SD error on the correction had to be increased to ±0.05 percent to cover the separate measurements.

The combined total error on all twelve factors was estimated to be equivalent to about ±0.156 percent of net sample cpm—much greater than that desired (±0.087 percent). Taking account of the counting errors, it was finally estimated that under the routine working conditions radiocarbon dates had an overall precision of ±0.31 percent, or about ±25 yrs.

In the evaluation of allowable errors, above, it was assumed, for ease of calculation, that all the errors followed a normal distribution; however as discussed, some of the errors were taken to be maximum errors, some were set at 1 SD level of an assumed normal distribution, and the remainder at 2 SD levels. As these assumptions may exaggerate the magnitude of the combined errors, a further examination of three factors has recently been made (since the work of Pearson and others, 1977). With the changes set out below the combined errors on the twelve factors now come to about ±0.07 to 0.08 percent of net sample cpm which is well within the target set. This, together with improved precision on reference standard and background obtained by continued accumulation of counts, now brings the overall precision to about ±0.25 percent, that is, ±20 yrs.

1. Variation of background with "purity." Continuous monitoring of the ^{14}C toluene vial showed a downward drift in the overall gain of the counter over a year, and the external source channels ratios over this period formed a normal distribution around the regression line. The error on "purity" can, therefore, be reduced to that calculated from the SD of the mean value. This is derived from at least 40 measurements and is, thus, less than 0.17 of the correction based on a single measurement, thus reducing the large background error of ±0.041 cpm to ±0.012 cpm. (It should perhaps be pointed out that the reduced error on "purity" compensates for the increased error arising in the correction of efficiency for "purity" following adoption of the curved relationship shown in fig. 1C, thus maintaining the estimated error on this correction at less than 0.005 percent of net cpm.)

2. Variation of background between vials. A closer examination of the combined distributions of all the background measurements has shown no significant differences between vials after a period of more than 4 yrs. Therefore, the original safeguard of 2 SD is not necessary. The error can now be reduced to 1 SD on a more precise mean value and then approaches the desired figure of ±0.025 percent of net sample cpm.

3. Correction for loss of sample benzene. Improvements in the accuracy of weighing due to the new vial caps brings the error on the correction down to ±0.021 percent of net sample count rate.

Perhaps the most interesting error source to emerge from this work is the effect of atmospheric pressure on background measurement. If no correction were made for atmospheric pressure, background measurements could not be held within a normal distribution, and it would no longer be appropriate to use a grand mean value accumulated from a long series of measurements because such a mean would relate to the average atmospheric pressure over the whole period of measurement. In addition, samples that were not measured over the same time period as their associated backgrounds would be biased. The magnitude of this bias depends on the variation in atmospheric pressure and on the ratio of sample volume to the total volume in the vial, because background counts are related to the total volume in the vial, while the sample counts are dependent on the amount of sample carbon in the form of benzene. It can be shown that a 20 mbar change in pressure can result in an inaccuracy of about 100 yrs in a half-life sample if the vial contains 5ml sample in a total volume of 15ml. Samples are sometimes counted in radiocarbon dating laboratories at an even greater dilution, and pressure changes may exceed 20 mbar, so that inaccuracies as large as 400 yrs are easily possible. Although the need to consider atmospheric pressure in gas counting has long been appreciated, recognition of the corresponding need in liquid scintillation systems is new. The importance of atmospheric pressure in this connection can probably be attributed to its inverse relationship with the intensity of cosmic radiation (Rochester, 1962; Lapointe and Rose, 1962), since cosmic radiation accounts for about half the background count rate observed.

Some of the other factors that have been investigated may also be the source of major errors, if no correction is made. Thus, it can be shown that failure to correct for the effect of variation in the weight of vial contents on vial efficiency and background could cause an inaccuracy of about 11 yrs, and if the error in weighing or pipetting vial contents exceeds ±5mg, the inaccuracy would increase markedly. Again, the error resulting from failure to operate continuously and precisely at balance point could introduce an error of 80 yrs. Failure to correct for errors in background measurement will become more serious if the sample is much diluted with inactive benzene. Those involved in radiocarbon dating should be alert to the various possible sources of error and recognize that the precision quoted on a date may be quite unrealistic if the error sources have not been investigated in detail.

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REFERENCES

Barker, H, Burleigh, R, and Meeks, N, 1969, British Museum natural radiocarbon measurements VI: Radiocarbon, v 11, p 278-294.

Birks, J B, 1970, Physics of the liquid scintillation process, *in* Bransome, E D (ed), The current status of liquid scintillation counting: New York, Grune and Shatton.

Callow, W J, Baker, M J, and Hassall, G I, 1965, National Physics Laboratory radiocarbon measurements III: Radiocarbon, v 7, p 156-161.

Dyer, A, 1974, An introduction to liquid scintillation counting: London, Heyden.

Lapointe, S M, and Rose, D C, 1962, A statistical analysis of the barometer coefficients for cosmic ray intensities: Canadian Jour Physics, v 40, p 687-697.

Pearson, G W, Pilcher, J R, Baillie, M G L, and Hillam, J, 1977, Absolute radiocarbon dating using a low altitude European tree-ring calibration: Nature, London, v 270, p 25-28.

Rochester, G D, 1962, Cosmic rays and meteorology: Royal Meteorolog Soc, v 88, p 369-381.