Technical Papers

Scintillation Counting of Natural Radiocarbon: I. The Counting Method

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Three technics of counting natural radiocarbon are now available: the screen-wall counter of Libby (*1, 2*), gas phase counters in the proportional or Geiger region (*3, 4*), and the scintillation counter (*5*). The first technic is proven and reliable, having been used successfully by a number of workers. The second and third offer special advantages. The gas counter has high efficiency with low background; especially with the use of acetylene (*4*), its sensitivity is very good. For small samples it will probably become the method of choice. The scintillation counter, with moderate efficiency, allows the effective use of large samples, and in principle has by far the greatest ultimate sensitivity of the three. An early attempt by the author (*6*) to develop this method was unsuccessful because of the limitations of the art at the time. Today phototubes of high efficiency and low noise, and liquid scintillators, are available. C^{14} and tritium have been measured at very low levels (*7*). This paper describes the counting technic developed in this laboratory for natural radiocarbon measurements.

The last two rows give a measure of the statistical precision of each method. It should be stressed that other experimental errors are possible, and that it is a matter of laboratory technic to reduce them to unimportance. Errors intrinsic in the method, such as isotopic fractionation, chemical exchange, and fluctuations in the natural abundance of C^{14} have proved to be relatively minor for the screen-wall technic. A notable improvement in accuracy will require reevaluation of these problems. It would be premature to claim that an error in dating of ±17 years can be achieved in practice. It should be added, however, that both the gas-counting and scintillation-counting methods should prove rather free of the contamination problems that have plagued a number of workers using the screen-wall method.

The chief limitation of the scintillation counter, since tubes of high photo-efficiency and low noise became available, has been the stability of the electronic system. The counting rates shown in column three of Table 1 are easy to achieve, and would allow far greater sensitivity than the screen-wall counter for measurement of C^{14}, if the precision were limited by statistical error. Background drifts of 2–3% make this increased sensitivity useless for precision work, however, and result in accuracy not appreciably better than that of known technics. Our method overcomes this problem while actually increasing the sensitivity of the instrument.

TABLE 1.

	Screen-wall counter a-c shielding (*1*)	Gas counter (acetylene) (*4*) a-c shielding	Scintillation counter 100-ml cell vol		
			33% ethanol no upper gate	33% ethanol pulse height disc.	80% paraffin pulse height disc.
Sample size	8 g	3 g	14.2 g	14.2 g	47 g
Counting efficiency	5.4%	75%	45%	25%	25%
Net sample counting rate	6.7 cpm	34.5 cpm	97 cpm	54 cpm	182 cpm
Net background counting rate	4.0 cpm	30.0 cpm	270 cpm	26 cpm	26 cpm
Statistical error, 2-day count	1.5%	0.7%	0.7%	0.46%	0.20%
Statistical error, in years, 2-day count (contemporary)	120	55	55	37	17
Maximum age limit ($S = 4\sigma$)	25,000 yr	30,000 yr	29,000 yr	34,000 yr	44,000 yr

Representative data for each method are shown in Table 1. The first two columns are based on data of Libby *et al.* (*1, 2*) and Crathorn (*4*). The third and fourth are data on natural radiocarbon obtained in this laboratory. The fifth shows values calculated from data on a sample of active polystyrene in a solution of 0.4% diphenyloxazole in 80% heptane-20% toluene. All are for 100-ml cell volume.

A block diagram of our apparatus is shown in Fig. 1. The tubes and sample cell (of 100-ml volume) are enclosed in a mercury shield, inside a deep-freeze held at − 20° C. The preamplifiers are attached to the shield. The gain of the preamplifiers is 30, and that of the main amplifiers is about 2500. This high overall external gain effectively eliminates what Hayes calls "light dark current," by reducing the internal gain of the phototubes and thus the number of light quanta they produce. The phototubes are DuMont type K1192, and show low noise with high sensitivity, when

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[1] The author is indebted to E. C. Anderson and F. N. Hayes for valuable discussions of this problem and for access to unpublished data and new scintillation materials.

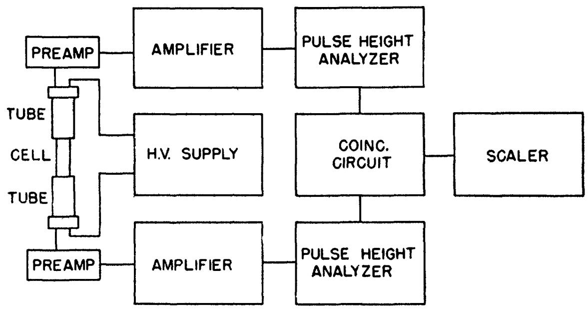

FIG. 1. Block diagram of counting apparatus.

the screen is connected with the first dynode. The speed of the amplifier is of the order of 1 μsec, and this effectively controls the time constants of the rest of the circuitry. Faster circuits were considered but not adopted, since at the noise levels now observed the accidental coincidence rate is negligible.

The pulse height analyzers are designed for wide-gate operation; the use of 6BN6 tubes allows a gate width of 85 v to be reached, which is desirable for C^{14} in view of its broad spectrum as observed in liquid scintillators.

All electronics, except the scaler, are run from a voltage-regulated supply, and are designed for stability and (in the case of the amplifier) excellent overload characteristics.

The liquid phosphor used is basically a solution of 0.4% diphenyloxazole (PPO) in toluene, with 20 ppm of diphenylhexatriene (DPHT) as a spectrum shifter. These materials show excellent compatibility with various organic liquids at $-20°$ C, whereas terphenyl, for example, is almost insoluble at this temperature. The basic phosphor solution is as good as any known. An increase in light output of 20–30% can be achieved by thorough flushing with N_2.[2] Further gains result from adding other components such as diphenyloxadiazole (PPD) to the solution but these are thus far too small to justify routine use.

Various organic liquids are compatible with this solution, without quenching the fluorescence excessively or causing precipitation of the phosphor. The solvent can be replaced with up to 40% methanol or ethanol, or up to 80% aliphatic hydrocarbon before the integrated C^{14} efficiency drops from 80 to 45%. Ketones and carbon disulphide act to quench the fluorescence. In our preliminary work ethanol has been used as sample since it is available from both fermentation and petroleum sources.

The background observed in this instrument, with upper gates not in use, is about 270 cpm. Only about 15 cpm of this can be due to mesons; the rest must arise from hard gamma contamination. The pulse heights are, on the average, several times higher than those due to C^{14}. It is this fact that makes pulse height discrimination so useful.

If, for example, the base line of the discriminator is set at 7 v, and the gate width at 60 v, the background and C^{14} count rates show a variation with high voltage as shown in Fig. 2. Since tube gain rises as a large power of the high voltage, simulating an exponential rise over a considerable range, this plot may be thought of as a reversed logarithmic pulse height spectrum for the two types of pulse. The peak in background comes at a considerably lower voltage than that of the C^{14} spectrum; the slight rise in the background rate at 1500 v is due to "light dark current."

The essential feature brought out by these curves is that the pulse height spectrum of the background has a broad minimum and the C^{14} spectrum a maximum at about the same voltage. Further, small adjustments of the phosphor efficiency can be made quite easily by bubbling N_2 or O_2 through the solution (the latter acting to quench the fluorescence and the former removing dissolved air). Thus the minimum of the background spectrum can be made to coincide with the maximum of the C^{14} spectrum. This operating point is called the balance point.

This is the most favorable operating voltage from the point of view of sensitivity and it is also the most stable position. Drifts in the high-voltage supply, preamplifiers, amplifiers, or pulse height analyzers are all compensated for, as all cause a proportional shift in the upper and lower gates. Even small changes in optical efficiency of the system operate in the same way.

When the apparatus is operated at the balance point, with a base of 7 v and gate width of 60 v, a solution of 1/3 "contemporary" ethanol and 2/3 phosphor solution shows a net effect of 54 cpm against a background of 20–26 cpm for a similar solution of "dead" ethanol, corresponding to 25% efficiency for C^{14}. A further, fortuitous element of stability is that this efficiency is almost independent of the integrated efficiency of the phosphor, over the range from 80% (characteristic of pure phosphor solution) to 45%. The efficiency can be checked accurately by comparison with a known standard added at the end of a run.

To test the capabilities of the apparatus, a series of three test samples was run. The first was pure living

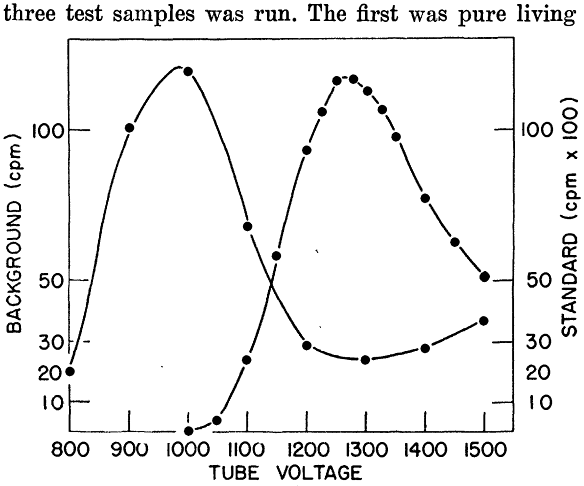

FIG. 2. Background and C^{14} count rate vs. tube voltage. The base level is 7 v and the gate width is 60 v.

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[2] This important effect was first called to our attention by Dr. B. Lionel Funt.

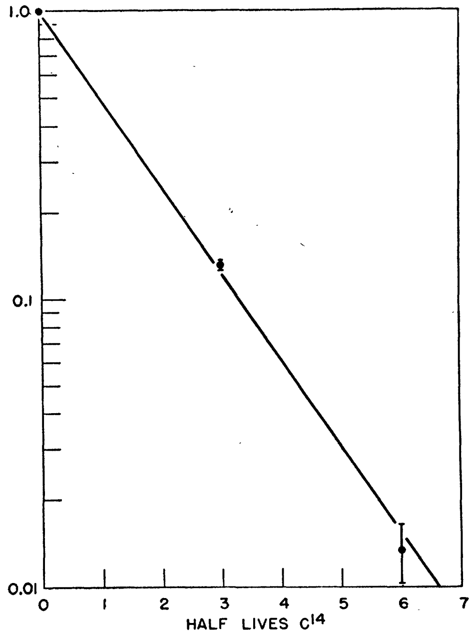

FIG. 3. Count rate vs. "age" for a series of synthetic samples. The line is drawn through the contemporary point with the theoretical slope.

alcohol, and the others were mixtures of 1/8 and 1/64 parts living alcohol with 7/8 and 63/64 parts dead alcohol, respectively. These samples simulate "ages" of 3 and 6 half-lives of C^{14}, respectively. The results are shown in Fig. 3, where the errors shown are the statistical counting errors (standard deviation) alone. The straight line represents the decay of C^{14}. It is seen that the samples agree within the statistical error. The counting data are internally consistent in the same way.

The value of the contemporary assay of natural C^{14} obtained from these data is 15.2 dpm/g carbon. This is in excellent agreement with previous data (*1*), but since our figure is based on an Oak Ridge standard of uncertain accuracy, its value is doubtful.

This method allows us to measure natural C^{14} to a precision of 0.46% in 48 hr, compared to 1.6% for the screen-wall counter technic. Six half-lives are well within reach, as the curve shows. A method for converting samples to aliphatic hydrocarbon is being worked out, so that solutions of good efficiency can be prepared that are 80% sample. This will allow a further extension of two half-lives. The cell size of 100 ml represents an arbitrary choice, and we believe that cells up to 1 liter or more in size are feasible with present equipment. Finally, the experiments of Cowan *et al.* (*8*) indicate that there is no natural limit to sample size, if sufficient starting material is available. We expect that it will be practical to extend the method to the point where its assumptions break down.

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Preliminary Investigations on the Role of Alfalfa Saponin in Ruminant Bloat

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Saponin has been suggested by several investigators (*1–5*) as being a contributing factor in the pathogenesis of ruminant bloat, especially "frothy" bloat. However, its exact role has been open to speculation for a number of years. Jacobson (*6*) isolated a compound from alfalfa that he regarded as a saponin as early as 1919. Boas and Steude (*7*), Jaretsky (*8*), Jaretsky and Lindner (*9*), Henrici (*5*), and Walter, Van Atta, Thompson, and Maclay (*10*) have now definitely established that at least 2 different saponins can be found in alfalfa. The only previous experiment described in the literature to ascertain the effect of feeding ruminants saponin actually derived from alfalfa was performed by Jacobson (*6*). Jacobson fed a sheep 19 g of his saponin preparation and reported that the animal suffered no ill effect. However, serious doubts have been raised as to the identity of Jacobson's product as a saponin because it contained combined nitrogen and did not hemolyze blood (*7, 8*).

The recovery of several pounds of a composite alfalfa saponin was undertaken at the Western Regional Research Laboratory to serve as starting material for isolation of the individual saponins and to provide a sufficient quantity for testing its activity as a factor in ruminant bloat.

This paper briefly describes the method used in the recovery of the alfalfa saponin and the results obtained with it in animal tests. The latter were carried out in the Animal and Poultry Husbandry Research Unit at the Agricultural Research Center.

Recovery of Alfalfa Saponins. The procedure for preparation of the composite alfalfa was as follows: Dehydrated alfalfa was extracted exhaustively with boiling water and the aqueous solution concentrated to about 50% solids *in vacuo*. Alcohol (95%) was added to yield an 80% alcohol solution which precipitated protein, salts, etc. The alcohol solution was decanted, evaporated *in vacuo* to 50% solids to remove alcohol, and the residue boiled with powdered cholesterol. The cholesterol-saponin addition product was filtered off,

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