molecules in which the axes of the successive planes were randomly oriented, but would be greater than that of a case in which the optical axes of the planes were all parallel. The latter situation places an upper limit on the absorption by the completely oriented element of 50 percent of the incident light. Until the detailed orientation of the visual purple molecules is known, this question cannot be resolved.

A density of 0.642 in the distal segment of the rod means that approximately 75 percent of the light incident on the rod segment is absorbed if its path is parallel to the axis of the rod segment. However, the retinal rods do not occur on the optical axis but are distributed peripherally. As a result, a beam of light which is less than the diameter of a rod in cross section may follow a path that will intersect several rods despite the curvature of the retina in the optic cup. If the beam falls at such an angle that it traverses the longest diagonal axis of a single rod, the probability of absorption would increase, for the path length through the rod is greater, and a somewhat thicker layer of photosensitive pigment would be traversed. In this case, the absorption would be 80 percent. If the beam intersected a closely packed, parallel bundle of rod segments at an angle of 45°, the absorption would be nearly 90 percent. Therefore, in species possessing a fovea, peripheral vision not only has the advantage of the higher absorption because of higher pigment concentration but also has the increased possibility of light gathering by the obliquity of the incident light.

As shown by Hecht *et al.* (*4*), a single quantum hit in each of only a small number of rods is required to produce a visual sensation in man at threshold. With absorptions by the individual elements of this order of magnitude or even considerably lower in the case of the mammalian eye, as suggested by Hubbard (*3*), the probability is high that the effective photochemical event will occur in the surface region of the receptor cell and that the resulting activated products will be in the optimal position for the initiation of the process that leads to membrane asymmetry and the initiation of an impulse, if indeed it can be assumed at this time that a mechanism as direct as this is involved in the initiation of the impulse.

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29 October 1956

Radiocarbon Age Estimates Obtained by an Improved Liquid Scintillation Technique

The physical and chemical techniques used in our laboratories for radiocarbon dating have already been described (*1*, *2*). The purpose of this work is to indicate an important modification in method and to report on the samples measured to this time (*3*).

In the liquid scintillation method of radiocarbon dating, the sample carbon is introduced into the sensitive volume as the solvent component of the scintillator or as a suitable diluent. Because of the low energy of the C^{14} beta spectrum and the resultant feeble light pulses, it is necessary to use a scintillator with as high a fluorescence efficiency as possible. This is particularly important for a single-channel counter used at ambient temperatures. We therefore first attempted the synthesis of the solvent component of the liquid scintillator from sample carbon (*1*), for this insures maximum luminescence output in the final scintillator solution.

On the other hand, for routine operation, the complexity of the chemical syntheses of such solvents as toluene and xylene suggests the use of an appropriate diluent whose chemical synthesis is less involved, and whose presence in the liquid scintillator does not appreciably reduce the luminescent output. In an earlier report (*2*), we showed that methanol could be used as a diluent in a liquid scintillator for the detection of natural radiocarbon with a 30-percent efficiency. An examination of Fig. 1 in that report shows, however, that labeled carbon concentrations of greater than 0.1 g/ml of scintillator are not feasible, for then the C^{14} spectrum and the photomultiplier noise spectrum overlap too markedly. A specially selected K1190 photomultiplier was used in this work. Subsequently, three of six C467 Dumont tubes tested have been found to give approximately the same low noise level as this selected experimental tube.

Recently (*4*) it has been shown that the use of naphthalene as the second solvent reduces the quenching action of many materials in liquid scintillators. Using this technique, we were able to introduce appreciable quantities of trimethyl borate (*5*) into a liquid scintillator without seriously affecting the efficiency of fluorescence. Since the methyl borate can be prepared quite readily from methanol, the possibility of its use as the labeled component for routine radiocarbon dating has been investigated.

The preparation of methanol from sample carbon was performed by procedures already described (*2*). The conversion of the methanol to methyl borate was accomplished by a modification of a procedure of Schlesinger *et al.* (*6*). In principle, the method involved the esterification of boric oxide with methanol and the separation of the resultant azeotrope. In a typical synthesis, 18.80 g (0.59 mole) of methanol was placed in a 100-ml flask fitted with a semimicro fractionating column, and 13.72 g of finely powdered boric oxide was added in four portions through a side arm. Following the addition of each portion, the contents of the reaction vessel were refluxed gently. Upon completion of the addition, the reaction mixture was refluxed a further 2 to 3 hours. The contents were then distilled through the column, and the methanol-methyl borate azeotrope was collected in a receiver immersed in dry ice. The azeotrope was then separated by rapid addition of 4.2

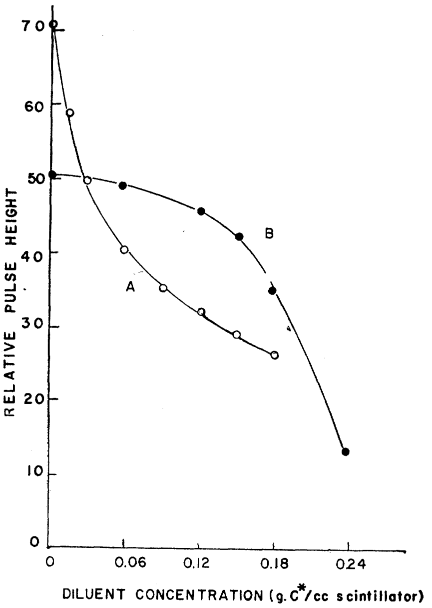

Fig. 1. Dilution curves showing pulse height, relative to anthracene at 100, as a function of diluent concentration expressed as grams of labelled carbon per milliliter of scintillator. *A*, Diluent methanol in solution of 4 g/lit of terphenyl and 0.1 g/lit of 1,4 di-2-(5-phenyloxazolyl)-benzene in xylene; *B*, diluent methyl borate in solution of 3 g/lit of phenylbiphenylyloxadiazole, and 70 g/lit of naphthalene in xylene.

g of dried anhydrous lithium chloride. The flask was vigorously agitated until two liquid layers were formed. The top layer, consisting of almost pure methyl borate, was separated in a micro separatory funnel. Further purification consisted of a distillation through a semimicro fractionating column, followed by a second lithium chloride separation, and finally a further fractional distillation. A boiling range of 67.5 to 68.5°C was observed, and a yield of 71 percent was obtained. The remaining methanol could be recycled for a further synthesis if required.

For comparison, the dilution curve for methyl borate is shown in Fig. 1. It is evident that despite the initially lower luminescence efficiency of the 2-phenyl-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) (3 g/lit), naphthalene (70 g/lit) scintillator, at C* concentrations greater than 0.03 g/ml this solution is superior to the methanol diluent. For methanol in a 20-ml cell, a net C^{14} counting rate of 7.39 ± 0.08 count/min over a background of 8.18 ± 0.05 count/min was the optimum counting rate obtained for contemporary carbon (*2*). For methyl borate with the same scintillator volume, we have realized a net C^{14} counting rate of 10.07 ± 0.08 count/min over a background of 4.26 ± 0.04 count/min. This improvement represents an extension in the range of the method of roughly 5000 years.

To date, six documented samples have been dated in our laboratories. The documentation was provided by the collector and is briefly summarized in Table 1. One sample (S-4) was dated by the methanol method because of the limited amount of sample available. The others were converted to trimethyl borate before counting. In each case, the unknown sample and the background dummy containing petrochemical carbon were alternated every 24 hours, thus bracketing each sample with two background counts. This procedure was facilitated by the use of two identical cells that had previously been carefully investigated for differences in radioactive content. The age assigned to any sample is the average age as determined by two 24-hour counts. The error assigned to any age is the statistical counting error. The results are summarized in Table 1.

Samples S-3 and S-4 have significance as part of a study by R. Lougeee of postglacial upthrusts on glacial seashores on either side of the Atlantic Ocean. According to N. R. Gadd, samples of wood from sample S-17 have previously been dated 11,050 ± 400 years by J. L. Kulp at Lamont Geological Observatory (sample L-190A), older than 30,840 years at Yale University (sample Y-242), and older than 40,000 years at the U.S. Geological Survey (sample W-189).

Samples S-6 and S-7 have been reported as greater than 38,000 years by the U.S. Geological Survey. Our results on samples S-6 and S-7 can be considered to be in good agreement with those obtained by other methods, but N. R. Gadd (*7*) suggests that geologic evidence would indicate that our sample S-17 should be much older than reported, and similar in age to samples S-6 and S-7.

Our experience with the afore-mentioned methods indicates that they are suitable for routine use in radiocarbon age estimates and offer certain attractive advantages in terms of simplicity of operation over other suggested scintillation techniques (*8*).

These methods also have sufficient accuracy to make them attractive in comparison to gas-counting techniques (*9*). The chemical syntheses of methyl borate are relatively simple. The electronic equipment is also of minimum complexity and avoids the use of anticoincidence equipment or refrigeration. However, in common with all other methods, problems of electronic drift and sample contamination may reduce the over-all precision below the statistically quoted limits. Increasing the scintillator volume would be expected to yield a higher precision but would necessitate the use of larger specimens and larger-scale syntheses.

Table 1. University of Manitoba radiocarbon dates.

Description	Sample No.	Age (yr)
Baie St. Catherine, Quebec. Driftwood from 13 to 20 ft below Mic Mac Terrace. Collected by R. Lougee, department of geography, Clark University.	S-4	3150 ± 130
Amherst, Nova Scotia. Stump from drowned forest in Bay of Fundy near Amherst. Collected by R. Lougee.	S-3	5300 ± 150
Missinaibi River, Ontario. Wood from a flat horizon of Missinaibi River area, from mouth of the Soweska River. Collected by O. L. Hughes, Geological Survey of Canada.	S-6	29,000 ± 1500
Missinaibi River, Ontario. Peat from the same area as sample S-6. Collected by O. L. Hughes.	S-7	38,500 ± 3500
St. Pierre-les-Becquets, Ontario. Wood. Collected by N. R. Gadd.	S-17	20,200 ± 800
Edmonton, Alberta. Alberta wood from the upper till of the Edmonton district. Collected by C. P. Gravenor, department of geology, University of Alberta.	S-15	21,600 ± 900

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16 November 1956

Acetylrhodopsin

The photosensitive pigment of rod vision, rhodopsin, is a chromoprotein composed in equimolar parts of the protein opsin and the carotenoid retinene (*1*). During the course of an investigation of some of its chemical properties, a successful attempt was made to acetylate rhodopsin. The acetylated pigment possesses spectral and photosensitive properties essentially identical with those of rhodopsin. Once bleached, however, the modified protein does not regenerate in the presence of the neo-b isomer of retinene as does bleached rhodopsin (*2*). The object of this paper is to describe the preparation and some of the properties of acetylated rhodopsin (*3*).

Cattle rhodopsin was prepared by methods previously described (*4, 5*). It was purified further by passage through columns of mixed-bed, ion-exchange resins, which remove amino acids and peptides in addition to other impurities of low molecular weight (*6*).

The optical properties of rhodopsin provide a useful index of purity. The absorption spectrum in aqueous digitonin solution has maxima at about 498 and 350 mμ, associated with the carotenoid chromophore, and a sharp peak at 278