

CHEMICAL TECHNIQUES FOR SCINTILLATION COUNTING OF NATURAL RADIOCARBON

by

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A Thesis submitted to the
Faculty of Graduate Studies
and Research in partial ful-
filment of the requirements
for the degree of Master of
Science



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ABSTRACT

A method for the age-measurement of archeological carbonaceous samples has been developed employing the liquid scintillation counter technique. This study represents the first successful attempt to incorporate the carbon from a sample, synthetically, in an organic compound which then served as the solvent in the liquid scintillator. With the electronic equipment available, the present upper limit of this method is 41,000 years.

In conjunction with the age-measurement method, studies were initiated leading to more efficient liquid scintillators. A marked quenching effect by oxygen dissolved in scintillation solutions was discovered. Nitrogen bubbling to displace the dissolved oxygen in all cases markedly increased the efficiency of the solutions.

ACKNOWLEDGEMENTS

In appreciation of the constant interest, valuable criticisms and guidance, the author expresses his most sincere thanks to Dr. B.L. Funt, who directed this research.

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PREFACE

In a series of research papers and a monograph (1), W.F. Libby in 1949 outlined a technique for the age-estimation of carbonaceous archeological samples using a specially designed, screen-wall type, Geiger counter. This was accomplished by synthetic conversion of the sample to elemental carbon and determination of its specific radioactivity. The radioactivity in these samples was caused by a naturally-occurring carbon isotope, C^{14} , present in amounts depending on the age of a particular sample.

The adaptation of liquid scintillation counters in a radiocarbon dating technique, with a significant improvement in accuracy and scope over that attainable by means of the Libby method, was the primary aim of this study. It will be shown that this technique has a number of important advantages over the screen-wall Geiger counter in the detection and analysis of low-energy radioactive emissions as characterized by C^{14} disintegrations.

This study was part of a joint project in conjunction with a Physics group (2) of this University. It was mainly concerned with the synthetic techniques involved in the incorporation of the carbon from a sample into compounds suitable as a source in the liquid scintillation counter. The adaptation of the scintillation counter to radiocarbon age measurements and the determination of the specific activity of a natural radiocarbon-bearing sample was the responsibility of the Physics group. An investigation of the properties of various organic solutions as scintillators was carried out as a co-operative project.

I. THEORETICAL INTRODUCTION

In his monograph (1), W.F. Libby has evaluated the theoretical and factual basis for radiocarbon dating. A resume of his data, and the assumptions made, will be considered.

It was discovered that C^{14} is produced in the earth's outer atmosphere by neutrons of thermal energies reacting with nitrogen:



These neutrons are the product of the impact of primary cosmic radiation on the earth's atmosphere and their secondary nature has been established (3). The radiocarbon thus produced was eventually found to be distributed throughout the earth's carbon reservoir; this includes the organic carbon of plant and animal life, inorganic carbonates found in rocks, and the carbonates, bicarbonates, and dissolved carbon dioxide in the earth's oceans.

The mode of transfer of the radiocarbon produced in the outer atmosphere is still largely a matter of speculation. Libby assumed that very shortly after the formation of a C^{14} atom it would be burned to carbon dioxide and, as such, found its way into the earth's carbon exchange reservoir. This seems to be a reasonable explanation, but is a matter of academic interest in this study. What is pertinent to this subject is the fact that the predicted value of the C^{12} to C^{14} ratio was found to be essentially correct. The radioisotope C^{14} disintegrates with the emission of a beta particle in the nuclear reaction:



The half-life of this radioactive decay process is known to be 5568 ± 30 years (4). After some reasonable period of time this radiocarbon would be present in some constant proportion to the ordinary carbon of the earth's exchange reservoir and equilibrium would exist in a living organism, with the rate of assimilation of new radiocarbon being equal to the rate of decay of the C^{14} already present in the organism. A similar equilibrium was found to exist in the $C^{12}:C^{14}$ ratio of the inorganic carbon of the earth's carbon reservoir. The bulk of the carbon in inorganic form is found in the oceans as dissolved carbonates.

Upon the death of an organism, plant or animal, the assimilation process would abruptly cease while the decay reaction of the radiocarbon already present would continue. Since the rate of disintegration, i.e., the half-life, of C^{14} has been found experimentally, then the determination of the specific activity of a carbonaceous specimen would yield an estimate of its age. The reliability of this age estimation would, of course, depend on the accuracy of the experimentally-determined radioactivity. To check the validity of his technique, Libby and his co-workers measured the activities of various carbonaceous samples using the C^{14} screen-wall Geiger counter method. The ages of these samples were known, all of them being in one of two groups: well authenticated archeological specimens, or wood samples from tree rings of known age. A graphical plot of the data obtained was in good agreement with the exponential decay curve of radiocarbon. This amply justified any assumption that Libby was forced to make in developing the theoretical basis for radiocarbon dating.

II. LIBBY METHOD

Measurement of the specific radioactivity of a carbon sample by the Libby screen-wall Geiger counter technique involves five steps: gross examination of the sample; combustion of the sample and collection of the products in liquid nitrogen traps; purification of the carbon dioxide obtained in the combustion; reduction of the CO_2 to elemental carbon, and finally, determination of the activity of the sample in a screen-wall Geiger counter.

The last step, namely, the actual counting of the activity of a sample will be described more fully than the other steps in order to compare it with the liquid scintillation counter technique used in this investigation.

Gross Examination

The importance of this preliminary step in the age determination of an archeological specimen cannot be over-emphasized. This is a basic requirement in the radiocarbon dating technique: the material under consideration must contain only the original carbon present in the organism at the time of its death.

The ideal sample for radiocarbon dating purposes would consist of elemental carbon, as found in charcoal or charred organic material. There would then be very little danger of exchange alteration due to chemical action, since the only natural reaction possible would be combustion. Libby found that organic material like wood, grasses, or peat, was quite trustworthy when it seemed to be in good physical condition. Where the archeological find was rich in carbonaceous material of the various types, a cross-check on the reliability of a more doubtful

source, as for example shell, could be made. It was found that under the conditions set forth, the reliability was quite satisfactory.

The order of reliability of material usually used for dating purposes was found by Libby to be:

- (a) Charcoal or charred organic material
- (b) Well-preserved wood
- (c) Grasses, cloth and peat
- (d) Well-preserved antler and similar hairy material
- (e) Well-preserved shell.

Combustion of Sample

The combustion of the sample was performed in the standard manner using a Vycor tube packed with copper oxide in the regular combustion furnace. Oxygen was used after purification to remove carbon dioxide and the combustion gases were condensed in liquid nitrogen traps.

Purification of Carbon Dioxide

The combustion gases were next bubbled through ammonium hydroxide solution to absorb the carbon dioxide. Calcium carbonate was precipitated by the addition of hot calcium chloride solution. After regeneration with acid and thorough drying, the carbon dioxide was stored in large bulbs.

Reduction of Carbon Dioxide to Carbon

The purified carbon dioxide was reduced to elemental carbon in a hot iron tube containing magnesium turnings. Treatment of the reduction mixture with acid left the residual carbon which was thoroughly washed and dried. This carbon sample was then stored in an air-tight vial to prevent undue absorption of atmospheric carbon dioxide.

Determination of Specific Activity

A special type of Geiger counter was developed by Libby to overcome the difficulty of changing from the sample or source to bare metal for the background count without varying the tube characteristics. This was accomplished by mounting the carbon sample as a very thin layer on the wall of a radial movable sleeve in the tube. A wire grid was then interposed between the tube wall and the counter wire and by controlling the potential on this "screen-wall" it operated essentially as the wall of the counter with respect to the center wire.

Radiations from the radiocarbon in the sample could then enter through the screen into the effective counter volume inclosed by the "screen-wall". Electrons emitted from the source were accelerated to the screen grid by a small "drag-in" potential. The sensitivity of the instrument to radiocarbon radiation was determined by using samples of known specific activity.

Shielding of the screen-wall Geiger counter was accomplished by means of a steel castle with eight-inch walls plus a layer of anti-coincidence counters placed around the central screen-wall Geiger counter tube.

The background rate for the unshielded screen-wall Geiger counter was found to be approximately 500 counts per minute. This background activity would be due to cosmic radiation plus laboratory contamination. With the shielding described, the background rate was reduced to five counts per minute. Libby and his co-workers found that a carbon sample of eight grams obtained from modern wood resulted in a counting rate of 6.7 c.p.m. above background.

III. THE SCINTILLATION COUNTER TECHNIQUE

The basic tool of this method for age-measurement is the scintillation counter employing an organic solution as the phosphor, a photoelectric multiplier to view the scintillator and the necessary attendant electronic circuitry for analysis and counting of the radioactive emissions occurring in the sample being measured.

The first attempt to employ a scintillating phosphor in conjunction with a photoelectric multiplier seems to have been described by Blau and Dreyfuss (5) in 1945. In that instance a screen of microcrystalline zinc sulfide was used. Further developments in this field followed rapidly and among others a comprehensive review of the subject was made by R.W. Pringle (6). In 1950, Reynolds et al. (7) discovered that certain dilute organic solutions made satisfactory scintillators. The theoretical aspects including mechanisms involved in the scintillation process will be discussed in greater detail in the chapter following.

In the present study, the application of the scintillation counter technique to the problem of age measurement, the carbon from a sample of archeological interest was incorporated synthetically in the methyl side chain of toluene; the toluene produced then served as the solvent in the liquid scintillator solution. In this way, the sample has become an integral part of the counting device and as will be discussed later in more detail, this is one of the main advantages of this technique over the Libby method.

Description of Counting Technique (2)

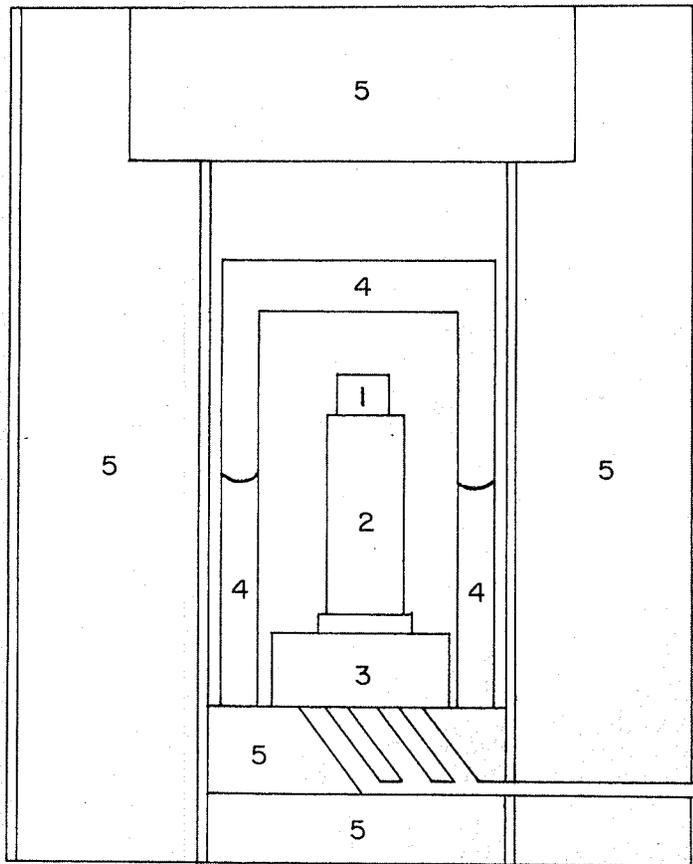
The glass cell containing approximately twenty ml. of the liquid scintillator with the photomultiplier were shielded in a lead castle

having a wall five inches thick. Additional shielding was provided by a can, shaped like a double-wall inverted cup, containing mercury. The glass cell containing the scintillator solution had a reflective coating of magnesium oxide over its whole surface, except for the bottom which was in contact with the light-sensitive end of the photo-tube. To insure light transmission from the cell to the photo-tube, a liberal layer of "Silicone" oil was applied to the bottom of the glass cell before positioning it firmly on the photo-tube. The electronic circuitry of the counting apparatus included a Dumont photomultiplier model K1190, in conjunction with a cathode follower, an amplifier with a gain of approximately 10^4 , a differential discriminator and a scaler unit. The cathode follower unit merely transmits the voltage pulses produced in the photomultiplier with a minimum of distortion. The amplifier, an Atomic Instruments model 204C, increases greatly the pulse amplification already attained in the photomultiplier. The differential discriminator, as its name implies, allows only pulses with voltages within definite pre-set limits to be registered on the scaler, a Glow Transfer model 162A. A block diagram of the apparatus is shown in Figure I.

The lead and mercury shielding eliminates a large fraction of the background radiation, and by judicious settings of the differential discriminator unit, most of the remaining background count is nullified.

Comparison with G.M. Counter

The accuracy attainable in the estimation of age of a sample by means of a dating method depends on the count ratio N/B , where N represents the number of counts per minute due to the labelled carbon in the sample and B is the number of counts per minute due to background radiation. It is desirable that this ratio be as large as possible because,



LEGEND

- 1.- LIQUID SCINTILLATOR
- 2.- PHOTOMULTIPLIER
- 3.- CATHODE FOLLOWER
- 4.- MERCURY SHIELD
- 5.- LEAD SHIELD

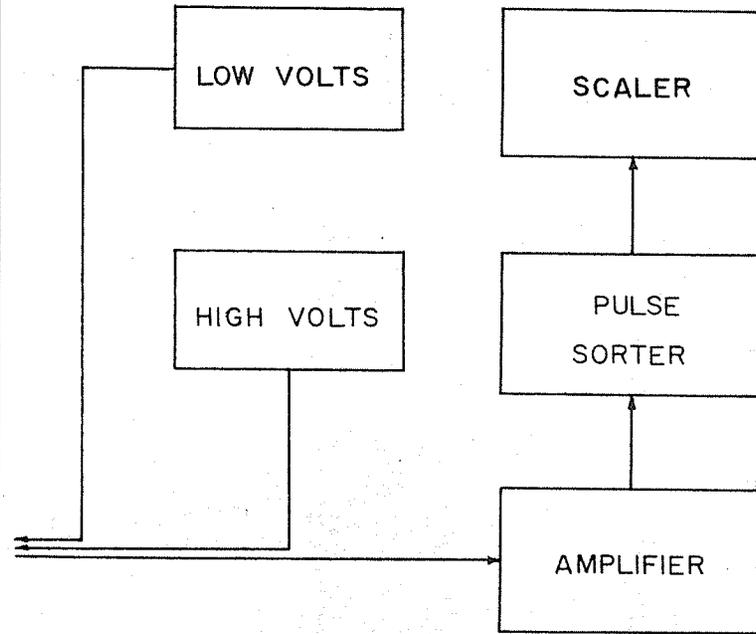


FIG. 1 : BLOCK DIAGRAM OF SCINTILLATION COUNTER.

for a particular sample, the accuracy of the measurement and the practical limit in age measurement are both directly related to the magnitude of this count ratio. Therefore N , the counting rate due to the sample, should be as large as possible and B , the counting rate caused by the background, as small as possible.

In the liquid scintillation counter the counting process occurs throughout the volume of the scintillator liquid. In the Geiger counter the disintegration particles from the surface layers only are counted. Since the beta particles emitted in the disintegration of C^{14} have low energies the particles produced in inner layers are absorbed before they can enter the counter. Consequently, the effective amount of sample available for the counting process is much greater when the scintillation counter technique is employed.

The geometry of the two instruments also favors a larger sample counting rate with the scintillation counter. In this case, there is a 4π counting whereas it is only 2π for the Geiger tube.

To reduce the background count, i.e., keeping B at a minimum, shielding by physical means such as mercury and lead, or steel, was employed with the scintillation counter technique as well as the screen-wall Geiger counter. In neither case was this sufficient to eliminate the high-energy cosmic radiation. The operating counter volume in the Geiger tube is comparatively large which makes shielding more difficult and is a quite serious defect since the Geiger counter records all primary nuclear events occurring within it. Also, the method of pulse discrimination possible in the scintillation counter is much simpler and relatively more effective in reducing background than the anti-coincidence counting employed with the screen-wall Geiger counter to eliminate radiation

not absorbed by the shield.

The scintillation counter has been shown to be inherently more stable than the Geiger tube; this, and the fact that the tube characteristics do not remain constant after changing samples in the Geiger tube, would result in better reproducibility of results when the scintillation counter is employed.

Lastly, the methods of synthesis available for sample preparation afford a greater probability of obtaining a contaminant-free source than was the case for the Libby method.

All these factors show the liquid scintillation counter technique to be superior to the screen-wall Geiger counter in the measurement of the activity of radiocarbon; (1) a greater effective carbon sample possible, (2) a detector efficiency up to 100% with 4π volume geometry, (3) size of detector makes cosmic ray background effects small as compared to the larger gas counter, (4) better reproducibility of results because of the inherent instability of the Geiger counter and a lesser possibility of source contamination.

IV. LIQUID SCINTILLATOR STUDIES

Need for Increased Efficiencies

In the final analysis, the scope and accuracy possible in this carbon dating technique would depend on the efficiency of the liquid scintillators used. This is evident since the energies of beta particles emitted by C^{14} have a maximum of 150 k.e.v. In 1952, the most efficient liquid scintillation solution reported contained 5 g./l. of p-terphenyl in xylene, which had a scintillation efficiency of 48% relative to solid anthracene (8).

Studies were initiated in an effort to obtain solutions with scintillation efficiencies greater than the ones reported. The effect of varying amounts of 2,5 diphenyloxazole on the scintillation properties of the standard terphenyl-toluene and terphenyl-xylene solutions was investigated and a very important quenching effect, due to oxygen dissolved in the scintillation solutions, was also discovered (9).

Theoretical Considerations

When charged nuclear particles pass through matter they cause molecular excitation and sometimes ionization in their path. This property is utilized in most of the instruments designed for the detection and analysis of sub-atomic particles. In some crystals and liquids the molecular excitations caused by an impinging particle are followed by a de-excitation process involving the emission of light in the visible or ultra-violet region. A photomultiplier tube viewing these scintillations converts them into electrical pulses which can then be amplified, analyzed and counted by the necessary electronic circuitry. This combination of apparatus essentially constitutes the modern scintillation counter. When