

CHEMICAL TECHNIQUES FOR SCINTILLATION COUNTING OF NATURAL RADIOCARBON

by

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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.

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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)

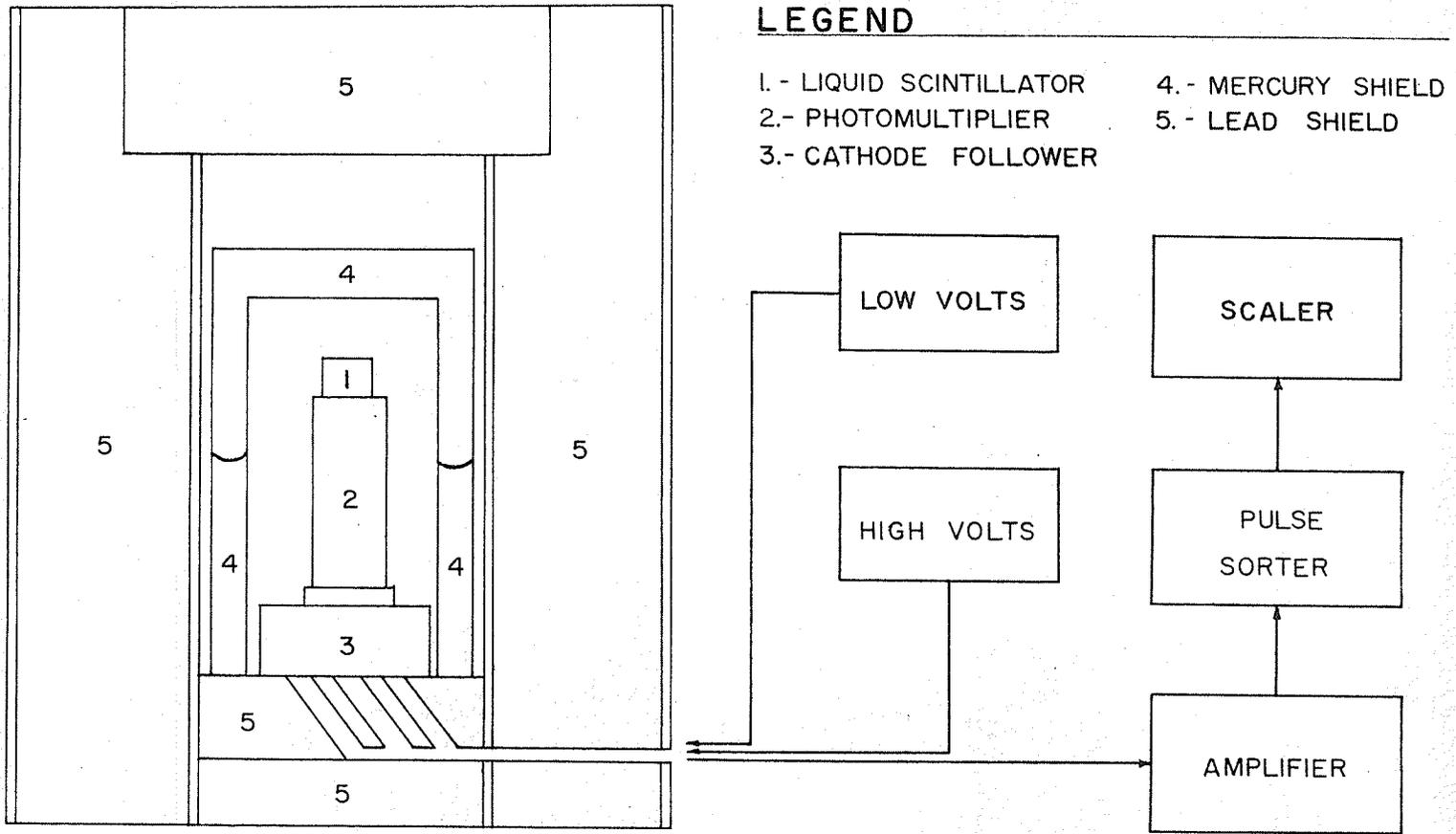
The glass cell containing approximately twenty ml. of the liquid scintillator with the photomultiplier were shielded in a lead castle

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

the scintillating phosphor is an organic solution the apparatus is termed a liquid scintillation counter.

In the comparatively short time since solutions of aromatic compounds have been used in scintillation counters, numerous investigations have been made in an effort to obtain the most efficient scintillation solutions and also to elucidate the basic mechanisms involved in the scintillation process (10). The energy system of an organic molecule can be represented by the regular potential energy diagram (11). Absorption of energy from an impinging particle on a light photon causes a transition in the molecule from the ground state to an excited energy level. The excess vibrational energy will be dissipated rapidly as heat and if the molecule is sufficiently stable it may return to the ground state with the emission of fluorescence. Since the band length is greater in the excited state the potential energy curve of this excited state will be shifted with a corresponding shift of the fluorescence spectrum to the long wavelength side of the absorption spectrum. The emissions observed almost invariably correspond to transitions from the lowest excited states to the ground states of the molecules involved. Therefore, there are actually three stages in the partial conversion of a particle's energy into a scintillation: (1) excitation of scintillation molecules, (2) degradation of excess electronic energy, and (3) emission of light from the lowest excited state. Only about ten per cent or less of the impinging particle's energy escapes as visible or ultra-violet radiation. The scintillation efficiency is defined as

$$\frac{N}{E} = \frac{q}{w} \quad (1)$$

where E is the energy of the particle, and N the number of

photons observed in a scintillation; w is the average energy required to produce one "fluorescence" excitation and q the fluorescence quantum efficiency. Equation (1) is strictly valid only for high-energy electrons and for scintillators not involving an activator. This, of course, is not the case with liquid scintillators. Kallmann and Furst (12) have shown that the fluorescence excitations produced in the solvent are transmitted to the solute molecules before quenching can occur in the solvent. Quenching occurs when there is an irradiationless transition of an excited molecule to its ground state with all the excitation energy being degraded as heat. Since the normal quenching of the solvent is bypassed, the quantum efficiency of the solvent seems greatly increased so that

$$\frac{N}{E} = \frac{q'}{w_0} \quad (2)$$

$$\text{with } q = \left(\frac{c}{1+c} \right) \left(\frac{q_1}{1+mc} \right)$$

where w_0 is the average energy required to produce one "fluorescence" excitation in the solvent; c is the molar concentration of the solute; m is the self-quenching constant of the solute; and $\frac{c}{1+c}$ is the ratio (probability of trapping in solute)/(probability of quenching in solvent). The concentration of the solute is low and therefore the energy of the particle is expended almost entirely on the solvent. The "effective" quantum efficiency of the solvent, q' , consists of two factors. The first factor, $\frac{c}{1+c}$ is the fraction of fluorescent excitation in the solvent that is transferred to the solute. The second factor, $\frac{q_1}{1+mc}$, is the quantum efficiency of the solute. It can be seen that it has a maximum value at low concentration and decreases with increasing concentration. Therefore equation (2) predicts a maximum value

of q' and also of N. Kallmann and Furst (13) have shown that this is in good agreement with experimental observations of light output versus concentration of the solute.

Experimental Procedure

In the liquid scintillator studies, the use of chemicals of exceptional purity was necessary since traces of unsuspected impurities were sometimes found to have a very deleterious effect on the scintillation properties of a particular solution. Reagent grade p-terphenyl was recrystallized twice from alcohol and then sublimed under low pressure. Later special "scintillation grade" p-terphenyl was obtained from the Pilot Chemical Company, Waltham, Massachusetts, while the 2,5 diphenyloxazole used came from Bios Chemical Laboratories, 17 West 60th Street, New York. On the other hand, reagent grade xylene from Merck Company, Montreal, was found to be satisfactory. Xylene which had been dried over sodium and distilled over a hundred-plate column did not prove to be superior as a solvent in the scintillator solutions. This was also found to be the case for the toluene used which was obtained from the same supplier.

The apparatus used in the liquid scintillator studies was essentially as described in the preceding section except for the fact that the photomultiplier assembly and the scintillation solution cell were mounted in a light-proof box without any shielding. The scintillations were produced by the gamma radiation from a Cs^{137} source. The pulse height or efficiency of a scintillator solution was determined relative to anthracene. For a particular solution a set of readings of counts per minute (c.p.m.) were recorded with the discriminator bias at a series of increasing voltage settings. A curve was then plotted

of counts per minute versus bias voltage. A similar procedure with an anthracene crystal mounted on the photomultiplier yielded a similar plot. For an arbitrary value of the c.p.m., the bias voltages were read from the two curves and the ratio of these gave the relative pulse height of the solution under consideration. For the experiments on the effect of dissolved oxygen on scintillator efficiencies, a fine capillary tube was sealed into the glass scintillation cell. The oxygen dissolved in the scintillator solution was then displaced by bubbling nitrogen through the capillary. The nitrogen was purified first by means of alkaline pyrogallol and magnesium perchlorate. A heated tube containing finely divided copper was also inserted in the bubbling line to remove any last traces of oxygen from the nitrogen, but this refinement did not result in any appreciable increase in scintillation efficiency.

Results

It was found that the displacement of oxygen by nitrogen bubbling improved the scintillator pulse height in every case, without exception. The nature of this improvement in scintillation efficiency for solutions of 3 g./l. p-terphenyl and 0.11 g./l. of 2,5 diphenyloxazole in xylene is illustrated graphically in Figure II using the data shown in Table I, part A. Also given in Table I, part B and graphically in Figure III, are the results obtained when bubbling oxygen through a solution that had previously been treated with nitrogen. As shown in Table I, part C, the fact that air bubbling of nitrogen-bubbled solutions depressed the scintillation efficiencies of solutions to their original values proved conclusively that oxygen was the quenching agent. The increase in light emission by the addition of diphenyloxazole to the

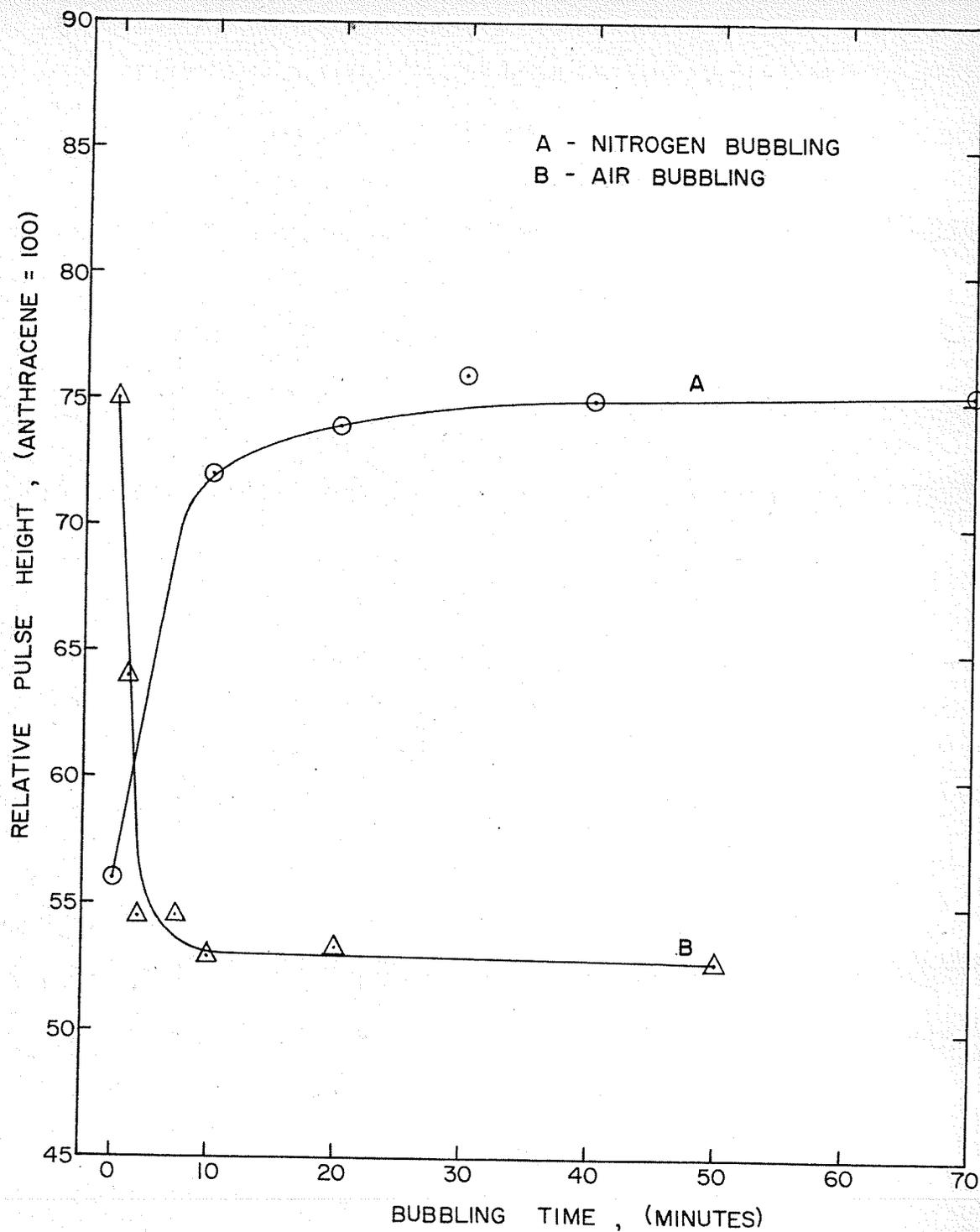


FIG. II : SCINTILLATION PULSE HEIGHT VS
DISPLACEMENT BUBBLING TIME FOR A
DIPHENYLOXAZOLE-TERPHENYL-XYLENE
SOLUTION .

TABLE I

Effect of Oxygen on Light Output

<u>A.</u> LIGHT OUTPUT (rel. to anthracene)	56%	72%	74%	76%	75%	75%	74%
NITROGEN Bubbling Time (mins.)	0	10	20	30	40	70	over- night
<u>B.</u> LIGHT OUTPUT (rel. to anthracene)	75%	61%	53%	35%	18%		
OXYGEN Bubbling Time (secs.)	0	10	20	60	100		
<u>C.</u> LIGHT OUTPUT (rel. to anthracene)	75%	64%	58%	54%	54%	53%	
AIR Bubbling Time (mins.)	0	1	2	3	5	10	

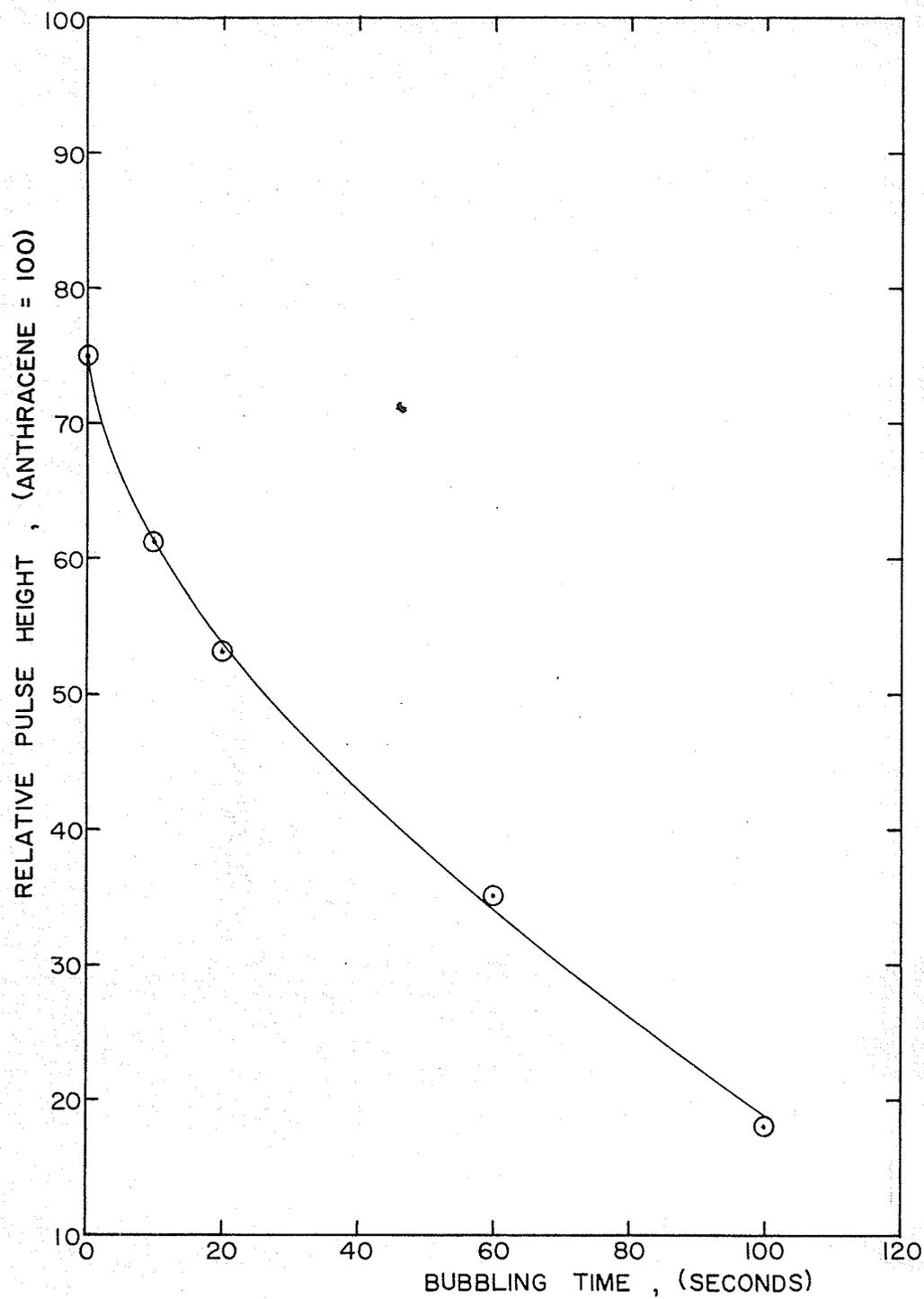


FIG. III : SCINTILLATION PULSE HEIGHT VS
OXYGEN BUBBLING TIME FOR A
DIPHENYLOXAZOLE-TERPHENYL-XYLENE
SOLUTION .

terphenyl-xylene solution as reported by Dr. J.R. Arnold in a private communication was also confirmed in these investigations. The data in Table II indicate the nature of this improvement in scintillation efficiency for increasing concentrations of diphenyloxazole in a 3 g./l. terphenyl-xylene solution. A concentration of one part in 10^6 of diphenyloxazole in the solution caused a remarkable enhancement in the light emission. It will also be observed that the removal of oxygen doubled the light output of the pure terphenyl-xylene solution.

For 3 g./l. terphenyl-xylene solutions, the increase in pulse height due to the combined effect of: removal of oxygen, plus the addition of small quantities of diphenyloxazole, is illustrated in Figure IV. A few representative results where solvents other than xylene were employed in scintillator solutions are also recorded in Table II. Refractionated p-xylene in solutions gave pulse heights comparable to those from xylene solutions.

Dr. R.W. Pringle has pointed out that the photomultiplier used in these experiments did not have an extended sensitivity in the ultra-violet region and therefore the light output of the liquids was not measured under circumstances as favorable as for the anthracene since the emission curve of the latter corresponded more closely with the sensitivity curve of the photocathode. It was estimated that an ultra-violet sensitive photomultiplier would so increase the relative efficiencies of the liquid scintillators studied that the best solutions after bubbling would appear superior to anthracene.

Discussion of Results

Studies by Bowen (14) on the quenching of fluorescence in organic solutions revealed that oxygen had a definite quenching effect. His

TABLE II

Effect of Nitrogen Bubbling on Various Scintillator Solutions

<u>Solvent</u>	<u>p-Terphenyl g./l.</u>	<u>Diphenyl- oxazole g./l.</u>	<u>Light Output (rel. to anthracene)</u>	
			<u>Unbubbled</u>	<u>Bubbled</u>
xylene	3.0	0	25%	50%
xylene	3.0	0.0196	51%	66%
xylene	3.0	0.0384	51%	69%
xylene	3.0	0.0741	53%	69%
xylene	3.0	0.110	54%	71%
xylene	3.0	0.200	55%	71%
xylene	3.0	1.00	54%	71%
xylene	3.0	5.00	50%	69%
p-xylene	3.0	0.10	35%	46%
p-xylene (refractionated)	3.0	0.10	54%	72%
o-xylene	4.0	0.10	38%	45%
toluene	4.0	0.10	28%	62%

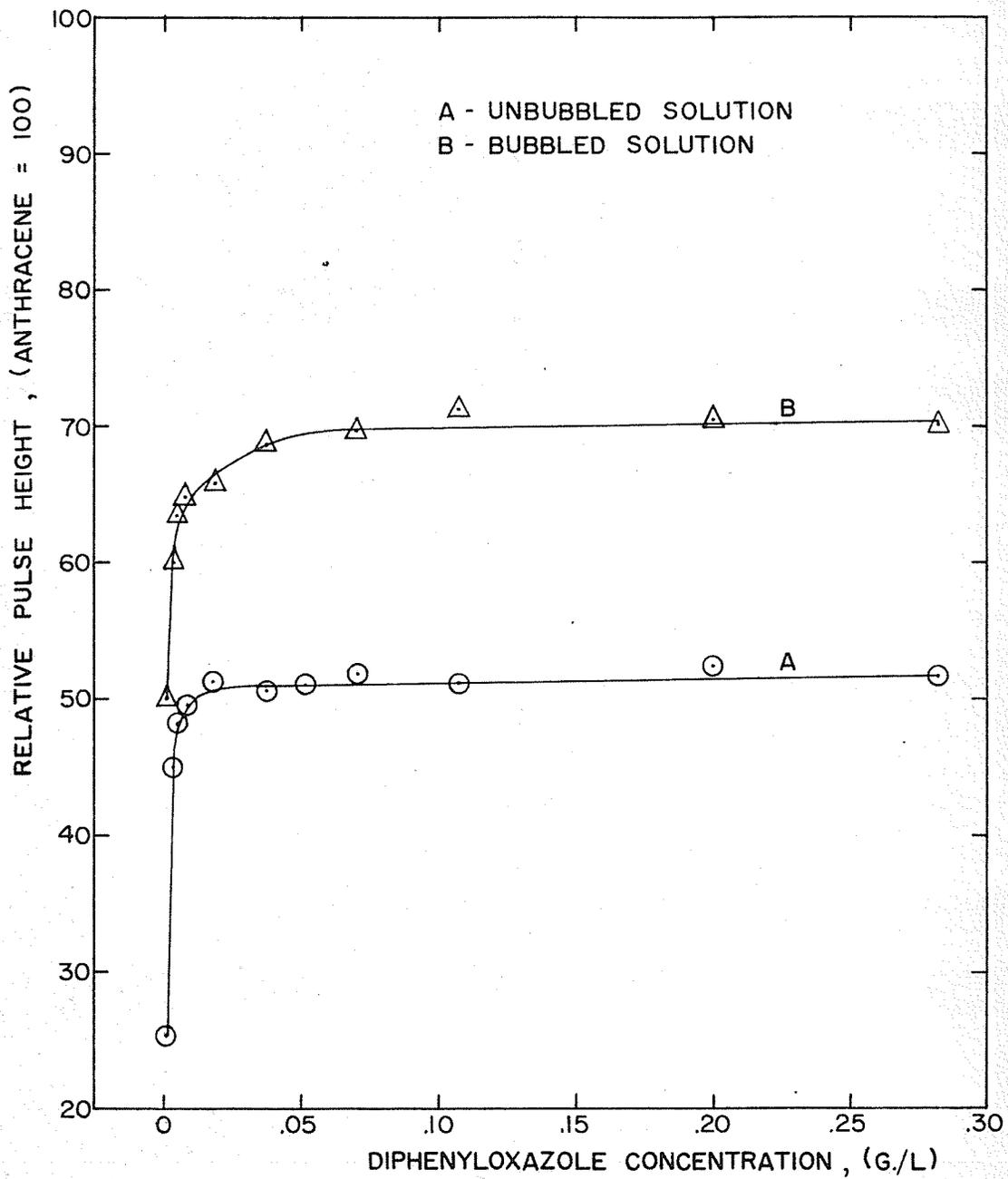


FIG. IV : SCINTILLATION PULSE HEIGHT VS
DIPHENYLOXAZOLE CONCENTRATION FOR
A 3G./L TERPHENYL-XYLENE SOLUTION.

solutions consisted of small concentrations of anthracene in various organic solvents. Anthracene has been shown to undergo photo-dimerization (15). There also is experimental evidence that it reacts photochemically with oxygen to form a peroxide (16). The mechanism of excitation and fluorescence de-excitation when organic solutions were irradiated with ultraviolet light was similar to that involved in the production of scintillations by nuclear particles impinging on the scintillator solution. Anthracene and p-terphenyl are both aromatic compounds. Therefore, the quenching by oxygen dissolved in a liquid scintillator probably is due to either photo-dimerization or photo-oxidation and possibly to both of these reactions. The very marked increase in quenching with a small amount of oxygen present as illustrated in Figure III would seem to indicate that photo-oxidation is the dominant quenching mechanism since it competes with the light emission process. In the case of photo-dimerization, a reduction of the number of activator molecules would occur, but this should result in a more gradual quenching since the scintillator efficiency of the regular 5 g./l. terphenyl-xylene solution does not decrease markedly with a slight decrease in the concentration of the terphenyl. The possibility of a metastable, excited oxygen molecule being formed has been removed by Gaffron's (17) investigation.

The magnitude of the increase in pulse height on addition of trace amounts of 2,5 diphenyloxazole to the scintillator solution indicates that the diphenyloxazole acts as a scintillation spectrum shifter. This shift in the light emission curve of the scintillations allows closer correspondence to the sensitivity curve of the photocathode. This effect of spectrum shifting is similar to that observed when traces of naphthacene are found in an impure anthracene scintillation crystal: the

emission spectrum is shifted from the blue of pure anthracene towards the green of naphthacene.

The combined effect on the pulse of nitrogen bubbling and diphenyloxazole addition to the terphenyl-xylene solution is illustrated in curve B of Figure IV. The improvement in light emission caused by increasing concentrations of diphenyloxazole in the unbubbled terphenyl-xylene solution is shown by curve A in Figure IV.

To obtain complete reproducibility of scintillation efficiency the removal of oxygen is necessary in all liquid scintillator experiments.

(1) Selection of appropriate liquid scintillator components. The objective is to select into the scintillator a mixture of low-boiling aromatic hydrocarbons. This will necessitate a micro-analysis in conjunction with each synthesis to determine the composition of each mixture obtained.

(2) Knowledge of optical densities of scintillator at various wavelengths required. This requires a study of the absorption spectra of the liquid scintillator.

(3) Determination of a design wavelength for the system. This will be done by the method of the liquid scintillator.

The design wavelength is determined by the method of the liquid scintillator. This will be done by the method of the liquid scintillator.

V. SYNTHETIC TECHNIQUES

Alternative Syntheses

Of necessity, the starting material in a synthesis of radio-carbon-bearing compounds suitable for use in a scintillation counter would be carbon dioxide or a carbonate obtained by combustion of the carbonaceous sample. Some practicable synthetic schemes with carbon dioxide or a carbonate as a starting material considered at the time this research program was initiated were:

(1) Aliphatic hydrocarbons by means of a Fischer-Tropach synthesis. The objections to this scheme were the uncertainty of the yields obtainable, and, more important, a product consisting of a variable mixture of low-boiling aliphatic hydrocarbons. This would necessitate a micro-combustion in conjunction with each synthesis to determine the composition of each mixture obtained.

(2) Reduction of carbon dioxide to methanol by means of lithium aluminum hydride. This synthesis was worthy of consideration since it had the great advantage of operative simplicity.

(3) Carbonation of a Grignard reagent under low pressure. This method was also characterized by its simplicity; the high yields reported; and elimination of possible contamination by atmospheric carbon dioxide.

There were few data available at this time on possible quenching effects in liquid scintillators of any of the compounds considered. With this in mind, the last of the three techniques outlined above was adopted as being the most promising of the alternatives under consideration. A large number of different acids could be produced with little or no variation in technique. If, at a later date, the organic acids were found

to have a quenching effect in liquid scintillation solutions, then step-wise reduction by means of LiAlH_4 of benzoic acid to toluene could be effected. Toluene was known to be one of the better solvents in liquid scintillators and would therefore serve the dual purpose of solvent and source in the liquid scintillation counter. Using this synthesis would, of course, result in a dilution of the sample carbon to one atom in seven. This procedure for the synthesis of toluene which had the sample carbon in the methyl side chain was therefore adopted.

After controlled combustion of the sample and precipitation of the carbon dioxide produced as barium carbonate, the toluene synthesis consisted of the four separate reactions:

- (1) Carbonation of phenyl magnesium bromide to benzoic acid;
- (2) Reduction of benzoic acid to benzyl alcohol by means of lithium aluminum hydride;
- (3) Conversion of benzyl alcohol to benzyl bromide using phosphorus and bromine;
- (4) Final reduction of the bromide to toluene using LiAlH_4 or a mixture of LiAlH_4 plus LiH although in this case the lithium hydride was not available.

These reactions were performed with test materials and any necessary modifications made. In the detailed description of each reaction, the yield quoted was that obtained in these preliminary experiments. In the integrated synthesis with a contemporary sample, it was found advisable to dispense with yield determinations in the intermediate reactions in order to conserve the products.

The high vacuum technique first used in the carbonation reaction was found to be applicable with high yields only when the amount of start-

ing material was of the order of 0.1 mole. On consultation with the Physics department it was decided that the end yield of toluene should be about thirty milliliters or 0.29 mole. The Grignard carbonation reaction was therefore performed at atmospheric pressure in a closed system with an automatic pressure-controlled carbon dioxide generator. The acquisition of an experimental photomultiplier tube with an exceptionally low thermionic noise level renewed the possibility of employing a diluent like methanol as a source material. Therefore a reduction of carbon dioxide to methanol using LiAlH_4 was also investigated. The two specifications for any particular reaction technique used in the syntheses were: the product contain no contaminating carbon, and also, the product yield be at least 80% and preferably higher. Most of the reactions used in these syntheses were comparatively well known, but usually modifications were necessary to make them conform to the criteria laid down above.

Purity of Chemicals

Unless otherwise stated, the chemicals used in the syntheses were of "reagent grade" as obtained from any one of the regular commercial supply firms. The lithium aluminum hydride for the reduction reactions was obtained from the Metal Hydrides Incorporated, 12 Congress Street, New York.

Preparation of the carbonate-free barium hydroxide entailed care in manipulation in order to exclude atmospheric carbon dioxide. A four-liter flask was used and the mixture of ordinary distilled water and excess "technical grade" hydroxide was heated to about 80°C . The flask was then stoppered using a two-hole rubber stopper with two glass tubes; one of them extending to the bottom of the flask. Ascarite guard tubes were placed on each of the tubes while the mixture cooled. A clear

saturated solution of barium hydroxide was obtained since the excess barium hydroxide crystallizing out carried down with it the insoluble barium carbonate. Calculations showed that the common ion effect depressed the solubility of barium carbonate in this saturated solution at 25°C. to 2.5×10^{-8} moles per liter. Carbon dioxide-free water was prepared by bubbling nitrogen through distilled water thus displacing dissolved carbon dioxide.

The dry ether used in the Grignard reaction and in the reductions with lithium aluminum hydride was prepared in one of several ways. If "anhydrous" ether had been purchased, last traces of water in the ether were removed by means of sodium wire. With "technical grade" ether preliminary drying with calcium chloride over a period of twenty-four hours was necessary to remove the bulk of the water and alcohol impurities. Final drying of the ether was then achieved again with sodium wire. The tetrahydrofuran, before use, was also treated with sodium wire as was the diethylcarbitol solvent in the methanol synthesis. Experiments later revealed that certain high alcohols present in the carbitol did not react appreciably with sodium and that treatment with methyl magnesium bromide or lithium aluminum hydride would be necessary to effect their removal.

The source of the bromobenzene used in the production of benzoic acid was checked to make sure that the carbon in the compound was "old" carbon; containing no radiocarbon. This difficulty was solved when it was ascertained that the bromobenzene had been produced from a petrochemical.

Combustion

Standard procedure was followed in the combustion of the sample. A three element macro-furnace with a Vycor tube was used. Temperature

control was maintained by having an iron-constantan thermocouple sealed into a pyrex tube beside the combustion tube in each of the three heating banks of the furnace. The temperature was maintained at about 500°C.

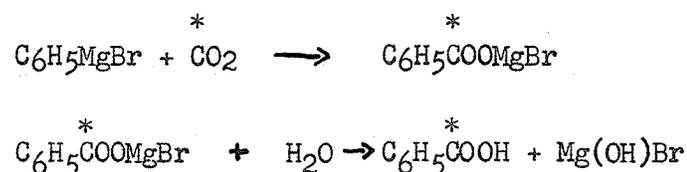
The Vycor tube was two thirds packed with copper oxide sticks and a plug of silver wool at each end of the CuO filling. Manitoba-grown beet sugar was found to be eminently suitable as a modern carbon sample. It was known to be at most a year old and was also of a high degree of purity. The oxygen for the combustion was pre-dried by means of concentrated sulfuric acid and magnesium perchlorate and any traces of carbon dioxide present removed with Ascarite. Pressure in the combustion train was kept slightly greater than atmospheric pressure. This effectively prevented contamination by atmospheric CO₂. Should there be any leaks, a small loss of combustion gases would occur, but this loss was insignificant. The sample was contained in two nickel boats with a capacity of about fifteen grams. The copper oxide prevented incomplete oxidation and the silver wool helped to remove sulfur oxides present. The combustion gases were bubbled through the barium hydroxide which precipitated the CO₂ as barium carbonate. It was found that with two bubblers, each of three-liter capacity, the CO₂ absorption was complete when the absorption solutions were stirred. "Trubore" ground glass stirrers were employed for this purpose.

On completion of a combustion the BaCO₃ in the absorbers was allowed to settle and the supernatant Ba(OH)₂ solution removed by suction. Carbon dioxide-free distilled water was then run into the absorption flasks and the supernatant solution again removed. This procedure was repeated until the supernatant liquid gave a negative test with CO₂. The BaCO₃ was then filtered with suction, dried at 110°C. and stored in air-

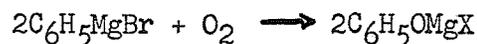
tight bottles to prevent adsorption of atmospheric carbon dioxide.

Labelled Benzoic Acid (18)

The well-known reaction between a Grignard reagent and carbon dioxide is utilized here as the first step in the synthetic chain having labelled toluene as the end product. The formation of benzoic acid from phenyl magnesium bromide with the carboxyl carbon coming from the sample is described by the equations:



The starred carbon in these equations denotes the position of the labelled carbon. Standard procedure in this reaction involves pouring the Grignard reagent over solid carbon dioxide. From our point of view this technique is useless since it is very wasteful of CO₂. A high vacuum technique was therefore used. The only side reaction with an undesirable product was the one between the Grignard reagent and oxygen to form phenol after hydrolysis:



The phenol being acidic would be precipitated with the benzoic acid when the reaction mixture was extracted with sodium hydroxide. To minimize the occurrence of side reactions, the carbonation was carried out at a low temperature.

The apparatus used for the carbonation is shown in Figure V. The barium carbonate was placed in flask B and concentrated sulfuric acid in the dropping funnel. The reaction vessel E contained the phenyl magnesium bromide. It was a three-necked one-liter flask. The pressure in the

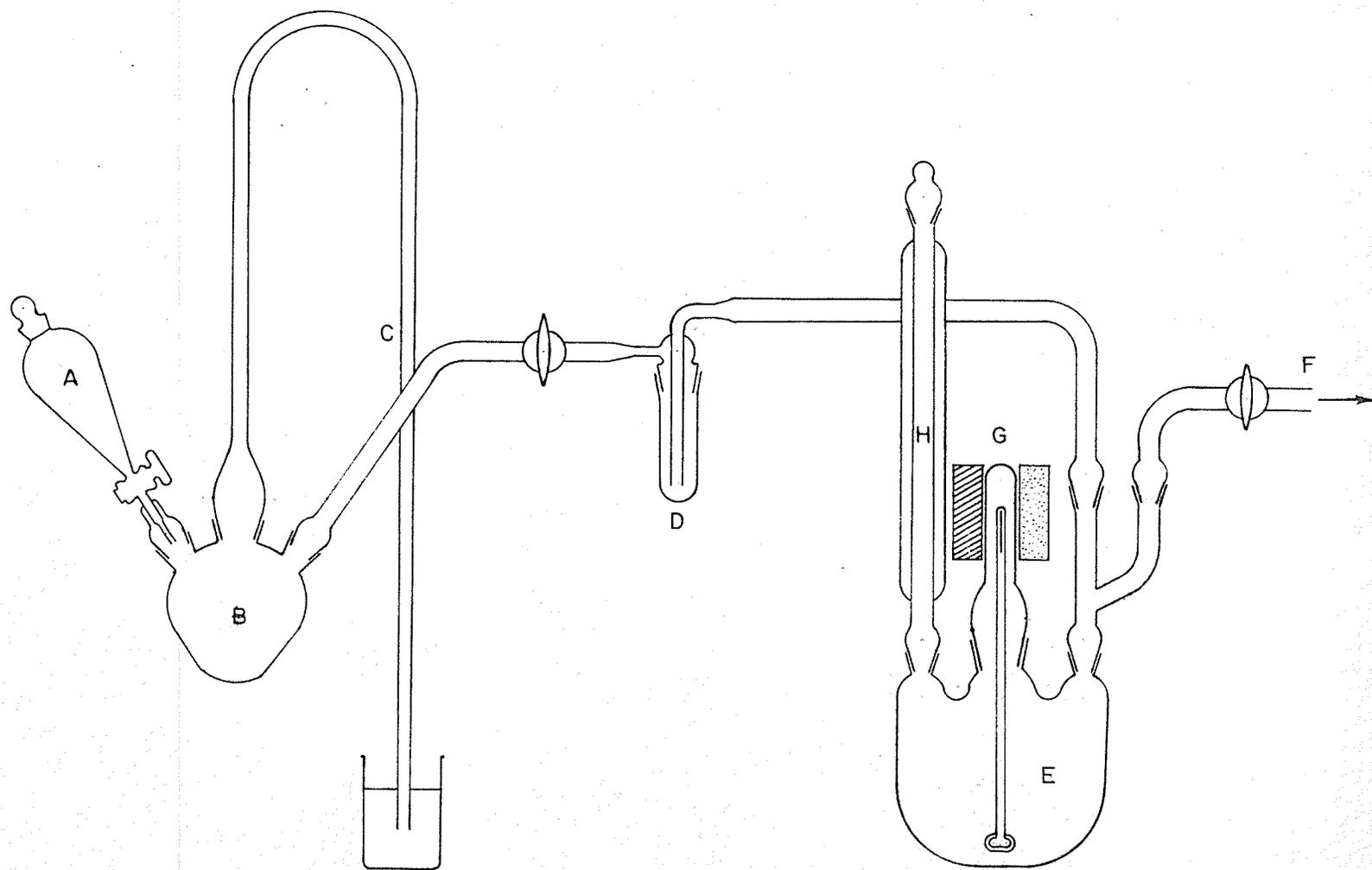


FIG. V : DIAGRAM OF LOW PRESSURE CARBONATION APPARATUS.

system during the reaction could be measured on the manometer C. The system was evacuated at the point F. A McLeod gauge and dry ice-acetone trap were in the vacuum line between the reaction system and the high vacuum oil pump. The reaction mixture was stirred by means of an electromagnet G. A soft iron nail in a glass tube fused on to the stirring rod kept the stirrer in vertical motion with an intermittent current in the coil. The phenyl magnesium bromide was prepared in the usual manner with phenyl bromide and magnesium turnings in dry ether. There was one refinement in the technique used (19); the reaction was carried out under a nitrogen atmosphere to prevent contamination of the reagent by atmospheric carbon dioxide. After placing the barium carbonate and concentrated sulfuric acid in the carbon dioxide generator, the system was evacuated, the pressure usually being of the order of one micron. After checking for leaks, the system was flushed with nitrogen and re-evacuated. The pressure in the system was then brought up to atmospheric pressure with nitrogen admitted through F. Transfer of the Grignard reagent-ether solution to the reaction flask was effected by pouring it into the condenser H. At the same time a flow of nitrogen was maintained through the reaction system. This effectively excluded atmospheric contamination. In a typical reaction, 20.0 g. of barium carbonate was placed in the generator and 300 ml. of a 0.5M phenyl magnesium bromide solution run into the reaction flask. This solution was then diluted with an extra 100 ml. of dry ethyl ether. A Dewar flask containing a dry ice-acetone slurry was then used to cool trap D in the system and the Grignard reagent cooled as much as possible using a large Dewar flask with dry ice-acetone. When the Grignard solution was cooled to -70°C . the system was again evacuated, the stopcock at F closed, thus isolating the reaction system.

The position of the mercury in the manometer was noted and the cooling mixture removed from the reaction vessel. The acid was then very slowly dropped on to the carbonate in the carbon dioxide generator. The pressure in the system was allowed to rise to approximately 50 cm. After starting the stirrer, a bath of an ice-salt mixture was placed under the reaction flask so that the temperature would not rise too rapidly during reaction. The carbon dioxide evolved was absorbed quite rapidly and after twenty minutes, at the most, the barium carbonate had been completely decomposed. To ensure complete decomposition, the barium sulfate mixture was heated gently with a small flame. At this stage, the pressure in the manometer registered about 60-65 cm. Hg. The ice-salt bath was then replaced by the dry ice-acetone slurry. The pressure in the system dropped very rapidly to within 2 cm. of the original value showing that the absorption of carbon dioxide was at least 98% complete. Nitrogen was now admitted to the system through the stopcock F, the reaction mixture allowed to warm up to about -20°C . and the mixture acidified with 50% sulfuric acid. The acid was added very slowly and carefully at the beginning since the hydrolysis of the excess Grignard reagent was very rapid and generated a large amount of heat. More water was added after the hydrolysis reaction had ceased to dissolve the magnesium salts present. The aqueous layer normally had a volume of about 200 ml. at this stage. The two layers were separated carefully and the benzoic acid was then carefully extracted from the ether layer with 30% sodium hydroxide. The benzoic acid could then be recovered in crystalline form by acidification of the sodium benzoate solution. The precipitate was filtered off and dried at 60°C . The yield was 10 g. of benzoic acid; 82% based on carbon dioxide. Three runs were carried out on this scale and in every case yields of 80-85%

based on carbonate were obtained. Since the radiocarbon dating method necessitated a fourfold increase in product, a reaction entailing an amount of barium carbonate of the order of 80 g. was attempted. The yield then dropped to 54%.

Since this method was not well adapted to large-scale synthesis, a different technique was evolved. The apparatus used is illustrated in Figure VI. The reaction vessel, J, was a ground-glass three-necked flask with a thermometer in one neck, a "Trubore" stirrer in the center joint and the entry tube from the carbon dioxide generator leading in to the third ground-glass joint. The bulb of the thermometer extended well into the reaction solution. The dropping funnel A contained 30% perchloric acid. This particular acid was used because barium perchlorate is readily soluble in water. The barium carbonate was placed in a 500 ml. suction flask, B, and had rubber tubing connections to the dropping funnel, the second tube leading to the upper entry of the funnel for purposes of pressure equalization in the funnel. A series of Drierite towers, F, and a dry ice-acetone trap, G, effectively dried the carbon dioxide generated. During a reaction run the stopcock on the funnel was adjusted to give an acid flow rate of about 25 drops a minute. As carbon dioxide was generated, the pressure in the closed system rose, forcing the mercury up in the left-hand arm of manometer D. At a pressure in the system approximately 3 cm. Hg greater than atmospheric pressure, contact was made with a wire in the manometer. This actuated the relay, at E, and stopped the acid flow by means of solenoid C. The rubber tubing connecting the generator and the dropping funnel was attached to the core of the solenoid so that the tube was pinched shut when the electric circuit was completed. This apparatus gave very satisfactory automatic control of carbon dioxide generation. The

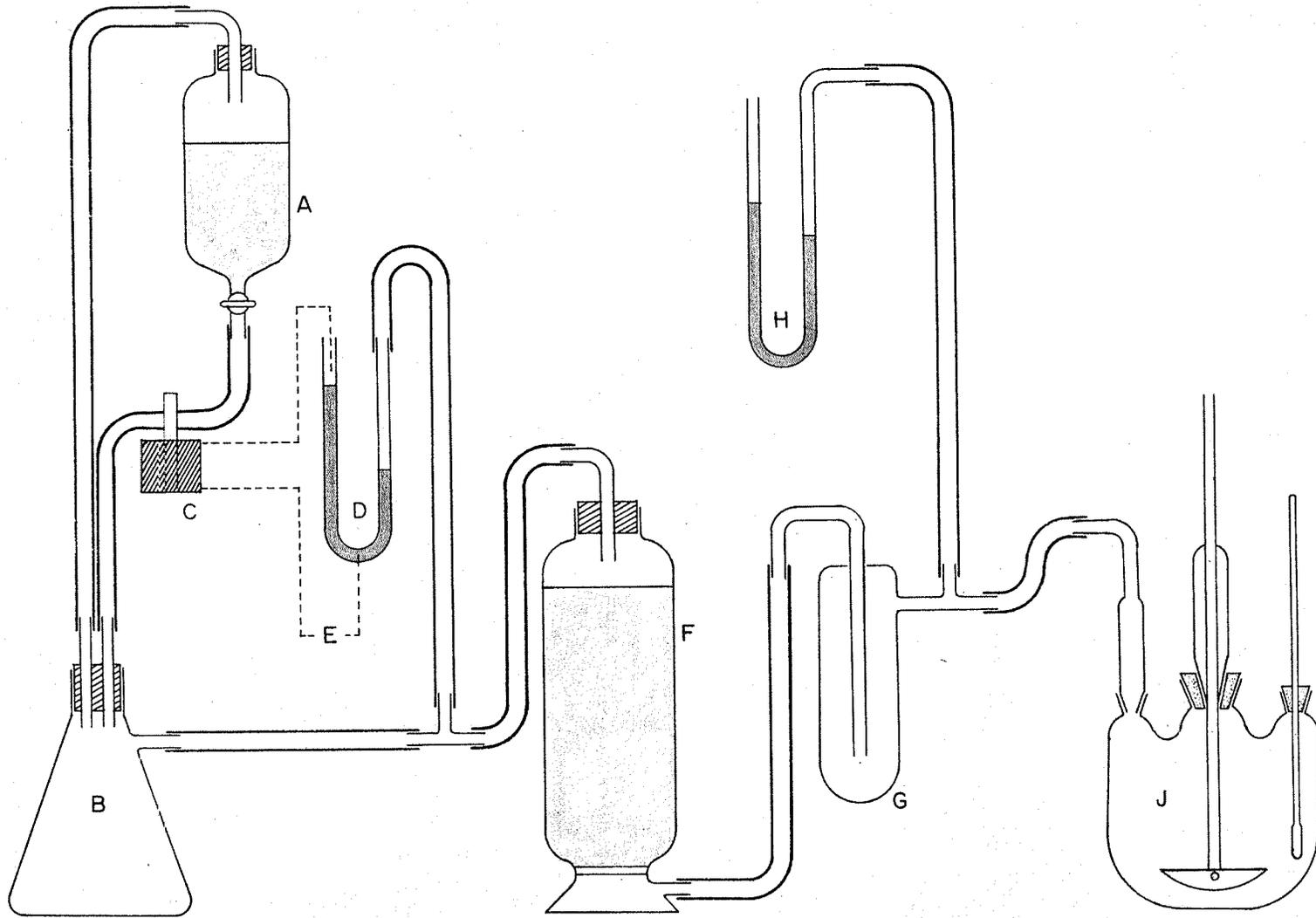
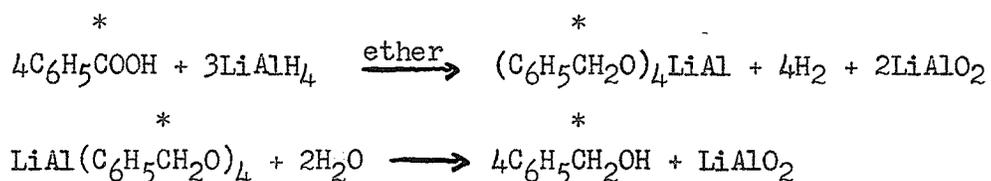


FIG. VI : DIAGRAM OF AUTOMATIC CARBONATION APPARATUS.

reaction vessel containing the Grignard reagent was cooled by means of an ice-salt mixture to about -10°C . Before a reaction was started, the whole system was flushed out very thoroughly with nitrogen. The manometer H served to give a convenient check on the pressure in the reaction vessel and made a leak in the system easily detectable. The reaction proceeded satisfactorily with a minimum of attention, and the automatic feature of this technique was one step towards reducing the time involved in synthesis and therefore anticipating a routine sample synthesis.

Reduction of Benzoic Acid (20)

The reduction of the acid to benzyl alcohol was effected by means of lithium aluminum hydride in ethyl ether. This reaction was characterized by its simplicity, freedom from side reaction and high yields. The lithium aluminum alcoholate formed in the reduction was decomposed by hydrolysis:

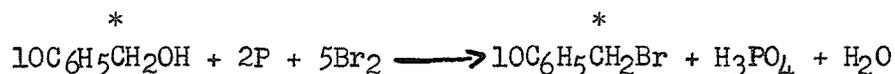


In a typical reaction, 0.26 moles of LiAlH_4 was dissolved in 400 ml. of dry ether by refluxing the mixture for three hours in a three-necked one-liter flask equipped with condenser, "Trubore" stirrer, and dropping funnel. The LiAlH_4 solution was prepared and the reaction carried out under a nitrogen atmosphere. This was done to exclude atmospheric moisture since LiAlH_4 reacts very readily with water to form hydrogen and lithium aluminate. The benzoic acid (0.21 moles) was dissolved in 250 ml. dry ether and slowly added from the funnel at a rate which produced a gentle reflux of the ether mixture in the reaction flask. Shortly after the addition of benzoic acid solution was complete, about 100 ml.

water was dropped slowly by means of the funnel into the reaction mixture. The heat of the reaction of water with the alcoholate and excess reagent again caused refluxing of the ether mixture. This reaction mixture was then poured into a beaker containing 200 ml. dilute sulfuric acid and crushed ice. Acidification was necessary to dissolve the amphoteric salts present. The two layers, water and ether, were then separated and the water layer washed twice with small portions of ether and then discarded. The ether washings were added to the main ether layer and the ether solution dried with anhydrous calcium sulfate (Drierite). The ether was distilled off with the residue consisting of benzyl alcohol. The yield based on benzoic acid was 85%, i.e., 19.0 g. of benzyl alcohol. No special difficulties were encountered and the scale on which the reaction was carried out depended only on the size of equipment used.

Bromination of Benzyl Alcohol (21).

The conversion of benzyl alcohol to benzyl bromide was carried out in the regular manner using red phosphorus and bromine. Due to the high boiling points of the alcohol and bromide, some minor modifications in technique were made. The reaction followed this equation:



The reaction was carried out in a three-necked 250 ml. flask equipped with a dropping funnel, a mercury sealed stirrer assembly, and a condenser connected to a fume trap. Since benzyl bromide is poisonous and a powerful lachrymator, the whole reaction was carried out in a fume hood. A mixture of 20 ml. (0.19 mole) of benzyl alcohol and 2 g. red phosphorus were placed in the reaction vessel and heated to about 80°C. Then 34 g. (0.21 mole) of bromine was slowly dropped into the hot alcohol-

phosphorus mixture. The rate of addition was such that there were no bromine fumes over the reaction mixture. After the addition of bromine had been completed, the temperature of the mixture was maintained at 80°C. for about three hours. Upon cooling to room temperature, the mixture was diluted with approximately 150 ml. of ether followed by about 100 ml. of dilute sodium bisulfite. The bisulfite oxidized any unreacted bromine to bromide. The unreacted solid phosphorus was filtered off, and the ether and water layers separated. The water layer was discarded after being washed with successive small portions of ether. These washings were added to the main ether solution which then was washed with dilute sodium carbonate to remove last traces of the bisulfite. The solution was dried carefully with Drierite and the ether distilled off. The yield of benzyl bromide was 20.1 ml. (88%).

Reduction of Benzyl Bromide to Toluene (22)

The reaction of alkyl halides with lithium aluminum hydride were found to be quite sluggish when carried out in refluxing ethyl ether. This difficulty was overcome by Blizzard et al. by using an ether with a higher boiling point, namely tetrahydrofuran. They also discovered that not all four of the hydrogen atoms in lithium aluminum hydride showed the same reactivity toward alkyl halides:



Of these, the first step was assumed to be more rapid than the second. Since aluminum hydride reacted with lithium hydride to produce lithium aluminum hydride, it also seemed reasonable and was found to be true that a mixture of lithium hydride and lithium aluminum hydride hydrogenated

the halide rapidly and to completion:



For the hydrogenolysis of benzyl chloride, yields of 98% were reported.

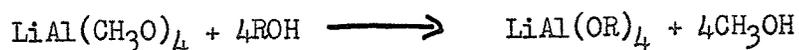
Lithium hydride was temporarily unavailable and therefore it was necessary to make do with lithium aluminum hydride alone in a 1:1 molecular ratio with the benzyl bromide. The reaction was carried out in a manner similar to the technique used in the reduction of benzoic acid. Instead of ethyl ether, tetrahydrofuran was used as a solvent for the lithium aluminum hydride and also for the benzyl bromide. For the reaction, 0.17 mole of each reactant was used; 6.5 g. of lithium aluminum hydride in 150 ml. of tetrahydrofuran and 29 g. of benzyl bromide in 250 ml. of tetrahydrofuran. After the addition of the benzyl bromide solution the reaction mixture was refluxed for three hours. Then 100 ml. of a 50/50 mixture of THF and water was slowly added; the rate of addition being regulated to maintain gentle reflux. The addition of 50 ml. of water was then effected, the reaction mixture being kept below 20°C. with an ice-water bath. After hydrolysis of the unreacted aluminum hydride, the large volume of solid salts made separation of the water and THF layers impossible. Attempts were made to dissolve the salts with 50% sulfuric acid. After the addition of enough acid to increase the volume of the water layer to 500 ml., the two layers were finally separated although some undissolved salts still remained. The bulk of the tetrahydrofuran was distilled off and distillation was discontinued when the temperature of the vapor rose to 70°C. Ether was then added to the solution and again a water layer separated. This phenomenon was due to the extreme solubility of tetrahydrofuran in water. The original water layer

was then washed with five separate portions of ether and these washings added to the main ether mixture. The small additional water layer was removed by means of a separatory funnel and the ether solution dried with Drierite and finally with sodium wire. The ether and residual tetrahydrofuran were distilled off and the benzyl alcohol distilled and redistilled once. At this stage, a yield of 12.2 g. of toluene was obtained. Based on benzyl bromide this was a relative yield of 76%. Once more, a great deal of difficulty was encountered in the procedure; this time in the removal of the last traces of tetrahydrofuran. Repeated distillations were unsuccessful and so a semi-micro fractionating column was built out of 7 mm. glass tubing filled with steel helices and insulated with cotton batting. The cotton batting was held in place by means of a large diameter glass tube which was then wrapped with one-inch heating tape. Fractional distillation in this still yielded pure toluene and the amount recovered was 9.1 g. or 10.5 ml. Although this synthesis was not at all satisfactory, the difficulties encountered would likely be lessened considerably when the recommended mixture of lithium hydride and lithium aluminum hydride was used for the hydrogenation.

Synthesis of Methanol (23)

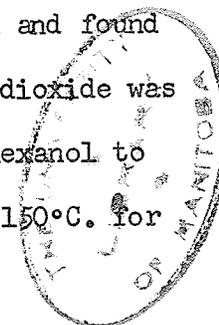
Depending on the conditions under which the reaction was performed, reduction of carbon dioxide by means of lithium aluminum hydride would result in different products. Carbon dioxide was rapidly absorbed by a lithium aluminum hydride-ether solution in the ratio of two moles of carbon dioxide per mole of hydride to form formaldehyde. With lithium aluminum hydride in excess, the reduction proceeded to the methanol stage. To obtain anhydrous methanol, the comparatively non-volatile diethylcarbitol was used as a solvent for the hydride. A high-boiling alcohol,

n-butylcarbitol was used to decompose the excess hydride and liberate the methanol:



(R = n-butylcarbityl)

This procedure was found to be very satisfactory by Nystrom, Yanko and Brown (23) and yields of 81% methanol were reported by them. In this synthesis the carbon dioxide was generated by dropping 30% perchloric acid slowly on to 20.0 g. (0.10 mole) of barium carbonate and was dried in a train consisting of a concentrated sulfuric acid bubbler, three Drierite towers, and a dry ice-acetone trap. The hydride solution was prepared by adding 5.8 g. (0.15 mole) of lithium aluminum hydride to 500 ml. of diethylcarbitol. There was vigorous reaction and a considerable volume of gas, presumably hydrogen, was evolved. The diethylcarbitol had been treated, prior to use, with sodium wire, and although it seemed unlikely, this reaction would seem to suggest the presence of water in the solvent. An additional 4 g. of the hydride was added and solution completed by heating the mixture, with stirring, for two hours. The reaction vessel was a one-liter three-necked flask equipped with Trubore stirrer and entry and exit gas tubes. The exit tube was guarded by a weighed Ascarite tube. The carbon dioxide was then bubbled into the solution using an equal volume of nitrogen as a carrier gas. When the carbon dioxide had been added, the Ascarite tube was re-weighed and found to have remained constant in weight. The absorption of carbon dioxide was therefore complete. After the addition of 400 ml. of 2-methylhexanol to the reaction solution, the mixture was heated to approximately 150°C. for



two hours. During this time the mixture was stirred and a continuous flow of nitrogen bubbled through the mixture. The carrier gas was then passed through a dry ice-acetone trap and the methanol condensed. The methanol obtained in the traps was redistilled at 32-33°C. The yield was 1.3 g. or 40%.

It was discovered that the diethylcarbitol contained some high-boiling alcohols which did not react to any appreciable extent with sodium. Therefore, before use the solvent should be treated with either lithium aluminum hydride or methyl magnesium bromide to remove the alcoholic impurities.

VI. RESULTS AND CONCLUSIONSExperimental Results

To indicate the degree of success attained in the development of this age measurement technique, some of the results obtained by Mr. Turchinetz are reported here. The synthetic toluene sample was progressively diluted to simulate specimens up to 34,300 years old. The apparatus used for the counting was essentially as illustrated in Figure I. The volume of the detector cell was twenty millimeters and the discriminator "gate" limits were set at 40-100 k.e.v. The background count over a forty-eight hour period was 3.33 c.p.m. The "ages" of the samples could be calculated using the known (25) specific activity of C^{14} and $\frac{N}{N_0} = e^{-kt}$, the disintegration law. The ratio N/N_0 then represents the weight of new toluene in the sample to the total sample weight. The counting data obtained and the "weight-estimated ages" of the increasingly diluted toluene samples are shown in Table III.

TABLE III

Counting Data and "Simulated Ages" of Toluene Samples

<u>Sample</u>	<u>Tot. Wt. (g.)</u>	<u>Wt. New Toluene (g.)</u>	<u>N/N_0</u>	<u>Wt. C[*] (g.)</u>	<u>"Age" years</u>	<u>Disintegration Rate d.p.m.</u>	<u>Net Counting Rate c.p.m.</u>	<u>Efficiency %</u>
1	17.50	1.98	0.11	0.26	16,500	3.91	1.86 ± 0.04	48
2	17.12	0.77	0.045	0.11	24,900	1.67	0.94 ± 0.04	56
3	16.89	0.24	0.014	0.032	34,300	0.48	0.30 ± 0.04	63

The counting efficiency was found to be approximately fifty per cent. A plot of the observed counting rates versus the "weight-estimated ages" was shown to be in good agreement with the slope of the half life curve of C^{14} (2). For an estimate of the upper limit of the measurement method, the statistical fluctuation of a forty-eight hour count was used. When the background count is indistinguishable from the statistical fluctuation, σ , then the error in the estimated age of a sample approaches infinity. Therefore a reasonable upper limit to the age which could be measured, and obtain meaningful results, would be an age equal to 2σ . Therefore, defining the maximum age as 2σ this limit was then calculated to be of the order of 41,000 years.

VII. CONTRIBUTIONS TO KNOWLEDGE

A radiocarbon dating method for archeological carbonaceous specimens has been developed to yield meaningful results to a maximum of 45,000 years. This limit could quite readily be extended to greater ages with improvement in electronic equipment, namely a photomultiplier tube having an extended sensitivity toward the ultra-violet region and also with a lower noise level. The results obtained compared very favorably with those obtained by Arnold (26) using a much more complex electronic assembly. It should also be noted that Arnold did not perform any chemical syntheses, but used C^{14} -bearing compounds obtained from natural sources. The present investigations resulted in the first successful attempt to incorporate carbon from archeological samples synthetically in compounds to be used directly in the scintillation counter.

Of major importance, not only in this technique, but in scintillation counting generally, was the discovery of a marked quenching effect by oxygen dissolved in scintillator solutions. Removal of the oxygen by nitrogen bubbling in all cases greatly enhanced the light output and in some cases even doubled the efficiency of solutions.

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