

CHEMICAL TECHNIQUES IN THE LIQUID
SCINTILLATION METHOD OF RADIOCARBON DATING

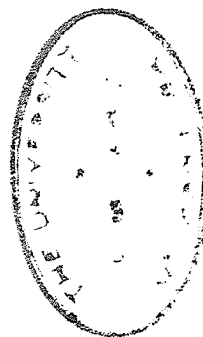
by

Steven Simeon Danyluk

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ABSTRACT

Two new methods suitable for routine determination of the radio-carbon activity in carbonaceous materials by the liquid scintillation method have been developed.

They involve the use of methanol and methyl borate, synthesized from sample carbon, as diluents in liquid scintillators of high fluorescence efficiency.

The methanol method is capable of yielding meaningful results to 30,000 years; the methyl borate technique gave results which indicate that this method can be of significance for samples up to 35,000 years.

Chemical procedures developed in the synthesis of methanol and methyl borate justify the adoption of these two methods for routine analysis.

Ages for six well documented samples of archeological interest were determined by means of the methanol and methyl borate methods.

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INTRODUCTION

The detection of radiocarbon in living matter in 1947⁽²⁾ spurred on investigation into its potentialities as a dating tool in the fields of archeology and geology.

With the publication of Libby's monograph⁽³⁵⁾ in 1952 the value of the radiocarbon dating method was firmly established and a new chapter in the field of geochronometry was opened.

Briefly, the method depends on a measurement of the beta activity of the C^{14} present in a specimen of natural carbonaceous material. This gives a measure of the radiocarbon to stable carbon ratio, and a comparison of the ratio to that for a sample of contemporary material permits an estimate of the age of the specimen to be made.

Libby and his colleagues⁽³⁵⁾ solved the problem of detection and measurement of the weak beta activity of C^{14} by measuring elementary carbon itself in the solid state mounted on the wall of a Geiger counter. By this method the ages of samples up to the order of 25,000 years were determined.

However, the low detection efficiency of screen wall counters, approximately 5%, and the handling of solid carbon samples inherent in this method warranted attempts to find a more efficient and sensitive technique of measurement.

The possibility of employing a proportional type counter using methane or carbon dioxide as the filling gas was suggested by Libby in his monograph. In 1952 Anderson and Freedman⁽²²⁾ reported the application

of a carbon dioxide filled proportional counter in radiocarbon dating measurements. Since then development of the CO_2 filled proportional counters has been rapid.^(22,15,16,21) In addition, the use of proportional counters filled with gases such as acetylene^(8,14,44), methane⁽⁹⁾ and ethane⁽²⁰⁾ has been reported. A range of 45,000 years has been obtained by Ferguson⁽²¹⁾ using a properly shielded CO_2 - filled proportional counter, and the possibility of extending this range even further by this technique is likely. The chief drawback of this method is the large detector volume presenting a serious problem in achieving low background counting rates and necessitating complicated shielding equipment.

Application of liquid scintillation counting to the measurement of natural radiocarbon was first reported by Hayes, et al⁽²⁷⁾ in 1953. In this method the sample carbon is incorporated into the liquid scintillator. Thus a detector of high sensitivity and excellent geometry is inherently present, and reduction of detector volume with the accompanying reduction in background counting rate is possible. The mass of shielding is greatly reduced and pulse height discrimination can be used to eliminate cosmic rays and much of the X-ray background.

Acetylene dissolved in a suitable liquid scintillator has been used in natural radiocarbon measurements⁽⁵⁾. Arnold⁽⁴⁾ in 1954, reported contemporary carbon counting rates of over 50 counts per minute, using "new" ethanol. However, this method suffered from involved chemical techniques and complicated counting assembly.

The synthesis of toluene from sample carbon and its use as the solvent in a liquid scintillator was reported in 1955.⁽²⁵⁾ Results

indicated that this method can be of significance for samples of age 45,000 years. By adequate shielding and pulse height discrimination a background counting rate of 3.34 cpm was obtained without photomultiplier cooling or coincidence-anticoincidence arrangements. The drawback of this method was the rather involved chemical synthesis of the toluene used.

In order to establish the suitability of the liquid scintillation method for routine analysis of natural radiocarbon, the development of a simple chemical procedure was essential.

With this problem in mind an alternative mode of attack involving the synthesis of a suitable diluent whose presence does not severely quench the liquid scintillator is possible. Success of this method depends, of course, on there being available liquid scintillators of high fluorescence efficiency. Fortunately such liquid scintillators have been developed⁽³⁸⁾.

In this investigation the successful synthesis of the diluent methanol and methyl borate from sample carbon and their adaption for routine analysis of natural radiocarbon will be described. Ages for six samples have been determined by these two methods. An analysis of the two methods will be given.

GENERAL CONSIDERATIONS

To simplify the presentation and to preserve continuity the discussion in this section will be carried out in the following order:

- A. Principles Underlying Radiocarbon Dating
- B. Chemical Synthesis of Diluents
 - (a) Methanol synthesis
 - (b) Methyl borate synthesis
- C. General Description
 - (a) Liquid scintillators and effects of diluents
 - (b) Cells
 - (c) Shielding and electronic circuitry

A. Principles Underlying Radiocarbon Dating

Investigations carried out by Agnew and co-workers⁽¹⁾ in 1947 clearly proved the correlation between the neutrons present in the upper atmosphere and the impingement of the primary cosmic radiation on the earth's atmosphere. The problem now was to determine in what manner the neutrons interacted with the atmosphere. It seems certain that shortly after formation the neutrons are either absorbed or lose their energy by collision finally attaining thermal energies.

From considerations of the thermal neutron capture cross-sections for the stable, naturally occurring isotopes of nitrogen and oxygen ($N^{14} = 1.7$ barns, $(n,p) N^{15} = 2.4 \times 10^{-5}$ barns (n,γ) ; $O^{17} = .5$ barns (n,α) ; $O^{16} = 1.7 \times 10^{-4}$ barns; $O^{18} = 2.1 \times 10^{-4}$ (n,γ) ;⁽⁴⁷⁾ and the per cent abundance of these isotopes ($N^{14} = 99.635$; $N^{15} = .365$; $O^{16} = 99.758$; $O^{17} = .0373$; $O^{18} = .203$)⁽²³⁾ Libby concluded that the reaction

leading to formation of radiocarbon, $N^{14} (n,p) C^{14}$, was the dominant one. Radioactive tritium may also be formed by energetic neutrons according to $N^{14} (n, H^3) C^{12}$, but the probability of this reaction is much less than that for the formation of radiocarbon. Thus, the impingement of cosmic rays on the atmosphere leads to the formation of radioactive C^{14} with a half life of 5568 years⁽³⁵⁾ and which decays with emission of a β particle.

If the average number of thermal neutrons generated per square centimeter of the earth's surface per second by the cosmic rays is \bar{Q} then the rate of production of C^{14} will also be given by \bar{Q} . If the further assumption is made that the cosmic ray flux has remained essentially the same over the last 10,000 or 15,000 years, then it follows that \bar{Q} is also equal to the rate of disintegration of the C^{14} on the earth. Evaluation of this \bar{Q} from experimental data available gives $\bar{Q} = 2.6$ per cm^2 per sec as the most likely value.

An estimate of the specific activity of the living carbon was achieved by Libby using the following line of reasoning. It seems certain that within a short time of its production in the atmosphere the C^{14} atom will have been oxidized to carbon dioxide which enters into the carbon exchange reservoir. Since the "turnover" time for the life cycle is short, (less than 1000 years) compared to the lifetime of a C^{14} atom, an atom will make several trips through this cycle during its lifetime, and consequently the distribution of radiocarbon throughout this reservoir will be quite uniform.

The amount of carbon in the exchange reservoir, following careful consideration of the complex biochemical problems involved, was

estimated by Libby as being 8.3 grams per square centimeter of the earth's surface. Thus the specific activity of the carbon in the exchange reservoir will be $\frac{2.6}{8.3} \times 60 = 18.8$ disintegrations per minute per gram. Experimental determinations of the specific activity carried out by Anderson and Libby⁽³⁾ gave a value of 16.6 ± 0.5 disintegrations per minute per gram and were regarded as confirmation of Libby's theory.

From consideration of the effects of isotopic fractionation the specific activity of biological carbon is expected to be lower by a factor of 10% than that of the inorganic carbon⁽³⁵⁾. Assay of the specific activity of contemporary plant carbon has given values of 15.3 ± 0.5 ⁽³⁵⁾, $14.5 - 14.8$ ⁽¹⁷⁾, 12.9 ± 0.2 ⁽²⁷⁾, 15.2 ⁽⁴⁾ and 12.5 ± 0.2 ⁽²¹⁾ disintegrations per minute per gram. Indications that a dilution of the atmospheric C^{14} concentration attributable to the introduction of large amounts of inactive CO_2 from combustion of petrochemical fuels into the atmosphere have been reported.⁽⁴⁴⁾

Bearing the original assumptions in mind, there exists at the present time, a complete balance between the rate of disintegration of radiocarbon atoms and the rate of assimilation of new radiocarbon atoms for all materials in the life-cycle. However, when the living organism is removed from this cycle by death, the assimilation process is stopped and only the disintegration process of the C^{14} remains. Decay of the activity will follow the exponential law $A = A_0 e^{-\lambda t}$, where A is the activity at time t , A_0 is the activity at time of death, and λ is the decay constant for C^{14} and is given by $\lambda = \ln 2 = \frac{.693}{5568} \text{ year}^{-1}$.

However, in the laboratory it is more convenient to measure the counting rate, R , in counts per minute where $R = cA$; c being a constant

depending on the nature of the detection instrument, efficiency for recording the particular radiation in that instrument, and geometrical arrangement of sample and detector. Thus, if R_0 is the counting rate in counts per minute per gram for a contemporary carbonaceous sample, and R is the counting rate for the sample of unknown age measured with the same apparatus, the age of the unknown sample, T , will be given by

$$\begin{aligned}
 R &= R_0 e^{-\lambda T} \\
 \text{or } T &= \frac{1}{\lambda} \ln \frac{(R_0)}{(R)} \\
 &= 8035 \ln \frac{(R_0)}{(R)} \text{ years}
 \end{aligned}$$

A brief description of the three methods, viz, (a) solid sample, (b) gas counting, (c) liquid scintillation counting, developed for the measurement of natural radiocarbon activities has been given in the preceding section. Detailed discussions of each method are available in the literature and a review has been given by Kulp.^(34a)

In the introduction it was mentioned that difficulties in the synthesis of an appropriate solvent limited the application of the liquid scintillation method for routine radiocarbon analysis. The alternative course of synthesizing a suitable diluent and combining it with a liquid scintillator of high fluorescence efficiency was therefore investigated.

Simplicity and high yields reported for the synthesis of methanol from carbon dioxide⁽³⁷⁾ immediately suggest its use as the diluent component. The suitability of methyl borate as the diluent arose following the reports of Kallman and Furst⁽²⁶⁾ that considerable quantities of this compound could be introduced into a liquid scintillator containing

naphthalene as the secondary solvent without affecting seriously the fluorescence efficiency of the scintillator. Methyl borate may be synthesized in one further step following the methanol synthesis.

B. Chemical synthesis of Diluents

(a) Methanol synthesis

Three methods for the preparation of carbon-labelled methanol from carbon dioxide have been described in the literature. Melville, Rachele, and Keller⁽³⁶⁾ converted CO_2 into KHCO_3 , which was reduced to potassium formate by hydrogen in the presence of palladium black. The formate was esterified by heating with methyl sulphate, and the ester converted into methanol by hydrogenolysis over a copper chromite catalyst. The overall yield on a 3 millimole scale was 73%. However, a 100% dilution with unlabelled material is inherent in this method.

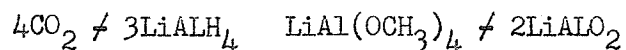
A second method involving the catalytic reduction of CO_2 to methanol at high temperatures and pressures has been described by Tolbert.⁽⁴⁵⁾ Yields of 81-86% on .025 mole scale were obtained, water being the major impurity. No dilution of the labelled material was possible in this method and except for the complicated equipment which would have to be assembled for the reduction of quantities of CO_2 of the order of a mole, this method would be quite suitable.

The third method, and the one chosen as the most feasible in conjunction with the present work on radiocarbon dating, was first described by Nystrom, Yanko, and Brown.⁽³⁷⁾ Carbon dioxide is reduced to methanol by a solution of lithium aluminum hydride in an involatile solvent, the methanol being recovered after alcoholysis of the resulting complex by a high boiling alcohol. These authors claimed an 81% yield of redistilled

material possessing high purity.

This method has been the subject of a detailed investigation on a micro scale by J.D. Cox et al⁽¹²⁾. The use of various solvents and alcohols for the reduction and alcoholysis steps respectively was investigated. These authors concluded that the best yields of methanol were obtained when tetrahydrofurfuroxytetrahydropyran was used as the solvent for the hydride and tetrahydrofurfuryl alcohol was employed in the decomposition and alcoholysis step. A further advantage gained in using these reagents, according to these authors, was the freedom from contamination with ethanol of the final product. When diethyl carbitol was employed as the solvent, it was shown that ethanol, probably due to the scission of the carbitol, was present as an impurity in the final product. Another, and perhaps more serious problem, encountered by Cox et al was the dilution of the labelled methanol with inactive methanol. This was ascribed to inactive CO₂ adsorbed on the LiAlH₄ used in preparing the initial hydride-carbitol solutions. A detailed discussion of the purity of the methanol samples synthesized is given on page 43, and a description of tests carried out to determine the extent of adsorbed CO₂ on the hydride is given on page 22 in section III.

Briefly, the first step, consisting of a reduction of the CO₂ by the hydride may be written as follows:



No detailed investigation of the course of the reduction has been published. Schlesinger and Finholt⁽⁴¹⁾ working with CO₂ in excess, found that 2 moles of CO₂ were absorbed per mole of hydride and that under these conditions a complex was formed which liberated formaldehyde on acidification.

Nystrom et al⁽³⁷⁾ working with 2-fold excess hydride noted reduction to methanol stage with the consumption of .75 mole of CO_2 . Cox et al⁽¹²⁾ demonstrated that even with 100% excess of hydride appreciable amounts of CO_2 are reduced no further than to formate and that formaldehyde is always present in the methanol liberated by alcoholysis of the complex. Thus, according to these authors, it is likely that the reduction proceeds via formate and formaldehyde. In view of the stoichiometry of the overall reaction it is probable that the methanol formed on alcoholysis is originally present as methoxide.

The second stage is a decomposition of the excess hydride followed by an alcoholysis of the complex methoxide to yield methanol, equations for the reactions being as follows:



where R = n-Butyl carbitol.

Of necessity, the starting material in the synthesis of methanol from any carbonaceous compound is CO_2 prepared by the combustion of the sample. The CO_2 is usually generated from BaCO_3 by acids or roasting.⁽¹⁰⁾

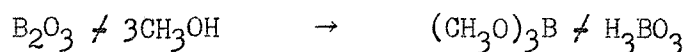
(b) Methyl borate synthesis

Since the first synthesis of methyl borate by Ebelman and Bouquet⁽¹⁸⁾ in 1846 many workers have described various procedures for preparing the ester.^(19,48) In most cases the techniques were relatively complicated and yields low. This was aggravated by the fact that the product, methyl borate, is obtained in the form of its azeotrope with methyl alcohol.

However, in 1953 Schlesinger and his co-workers⁽⁴²⁾ developed a

method of obtaining methyl borate of almost 100% purity in yields of 90% or better by one of several alternative routes. These authors also described the properties of the methanol-methyl borate azeotrope. In addition three methods of separating the methyl borate from the azeotrope were discussed.

It would appear possible that the reaction of one mole of boric oxide with three moles of methanol would lead to the formation of one mole of methyl borate free from methanol according to the equation



Actually, however, Schlesinger, et al,⁽⁴²⁾ found that the distillate consisted of the azeotrope in 71.6% yield. When four moles of methanol were used, three moles for the esterification and one mole for the azeotrope, per mole of boric oxide, the yield of methyl borate as azeotrope was 99.4%.

Further using the data of Schlesinger, when the mole ratio of methanol to boric oxide was three to one, the amount of unreacted methanol left was 20.1%; for a mole ratio of four to one, the amount of unreacted methanol was 36.9%.

Since in the present case the maximum conversion of the methyl alcohol to the methyl borate was of prime importance, the latter methanol to boric oxide ratio was ruled out. Thus, although the yields of methyl borate, based on the amount of boron utilized, were much less, there was not a large excess of methyl alcohol left unreacted.

Of the three procedures available for the separation of the ester from the azeotrope viz. (1) washing the azeotrope with sulphur acid, (2) Azeotropic distillation with carbon disulphide, (3) treatment with salts, the third method is considered best by Schlesinger et al⁽⁴²⁾. It consists

of the addition of salt such as lithium chloride to the azeotrope. The azeotrope separates into two layers; the upper layer containing methyl borate of 99.7% purity.

An important advantage gained in employing lithium chloride to separate the azeotrope is the ability to recover practically pure methanol by a simple distillation of the lower lithium chloride layer.

C. General Description

(a) Liquid scintillators and effects of diluents

Liquid scintillators are composed essentially of a scintillating phosphor (p-terphenyl) as the primary detector, and a solvent such as xylene or toluene which absorbs the energy initially. In addition to the use of a primary fluorescent solute as activator the addition of very small amounts of a secondary solute, (1,4 - di-(2-(5 phenyloxazolyl)-benzene), provides a better match to the photomultiplier sensitivity. These secondary solutes, called wave length shifters, absorb fluorescence from the primary solute and remit it at longer wave lengths.

In the diluent method of counting C^{14} a suitable solvent, called a diluent, whose presence does not quench severely the fluorescence efficiency of the primary scintillator solution, is added directly to the primary liquid scintillator. Thus one of the problems involved, apart from electronic stability and chemical synthesis, is the availability of a basic liquid scintillator solution the pulse height efficiency of which should be high enough so that the addition of a diluent is feasible. This difficulty is especially evident when methanol is the diluent, and to a lesser degree in the case of methyl borate.

Quenching of the fluorescence efficiency of a solution by the methanol was quite pronounced, as can be seen from Figure I curve A, where the diluent concentration was plotted against pulse height efficiency relative to anthracene. Although addition of methyl borate also decreased the fluorescence efficiency of a liquid scintillator, the effect shown in Figure I curve B was not quite as severe as that due to methanol. By employing a secondary solvent such as naphthalene⁽²⁶⁾ it is possible to introduce into the scintillator a much larger quantity of methyl borate without decreasing the fluorescence efficiency as markedly as in the case of methanol.

The problem of increasing the fluorescence efficiencies of liquid scintillators has been the subject of intensive investigation. New primary solutes, which may be referred to as "phenyloxazoles" developed by Hayes et al (28, 31) were found to increase the light output of solutions considerably. An important quenching effect attributable to dissolved oxygen was discovered in 1953.⁽³⁸⁾ Bubbling of dry, oxygen-free nitrogen through the solutions was found to increase the fluorescence efficiency of liquid scintillators by as much as fifty per cent, while bubbling with oxygen reversed this effect in every case. Oxygen-quenching of liquid scintillators has been investigated extensively by Funt and Neparko⁽²⁴⁾ and a quenching mechanism proposed. In 1955 Hayes and co-workers⁽³⁰⁾ reported bubbling of liquid scintillators with pure argon increased the fluorescence efficiencies in a manner analogous to that effected by nitrogen bubbling.

A detailed description of the techniques and liquid scintillator solutions used to determine the dilution curves is given in the experimental section.

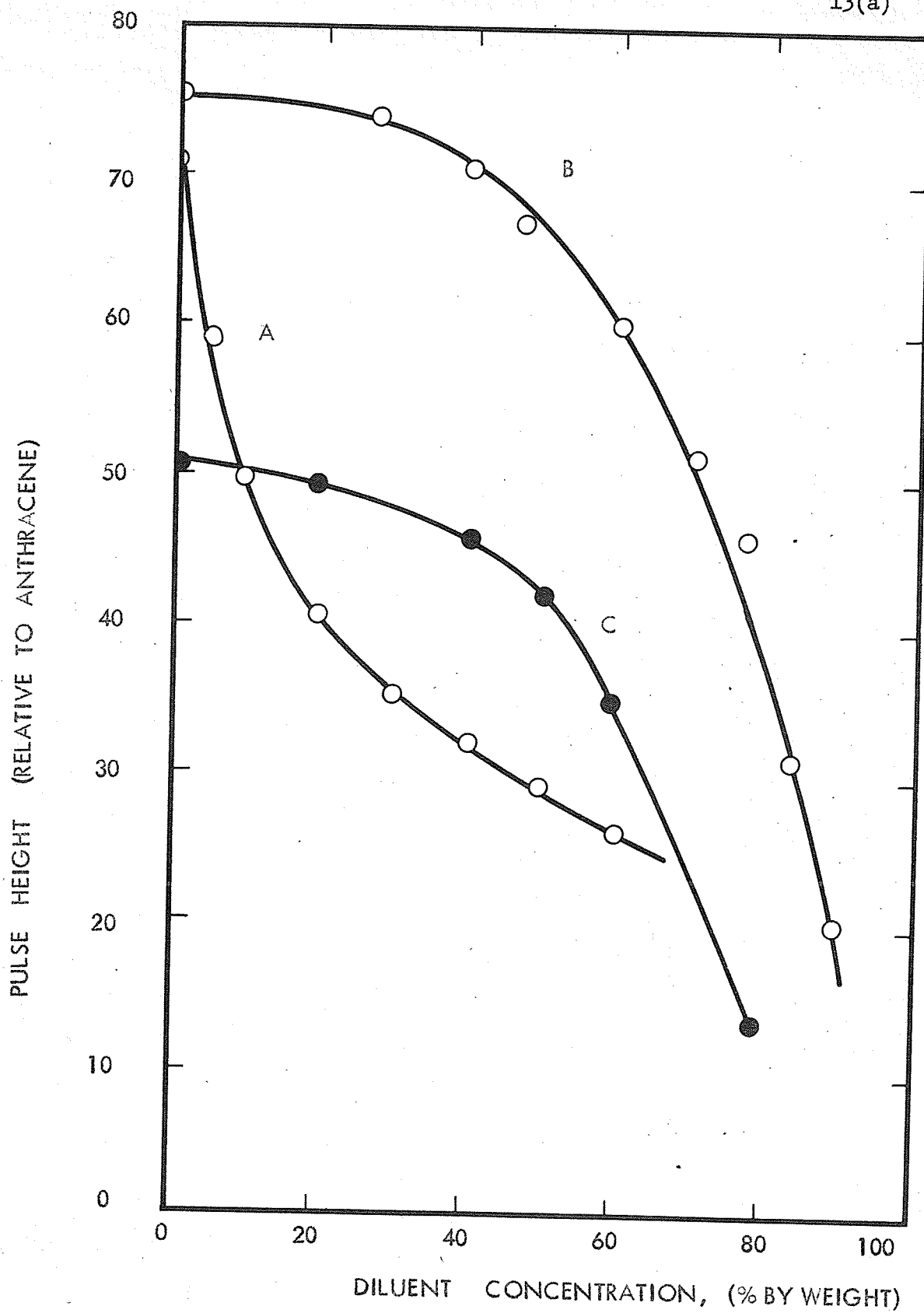


FIG. 1 EFFECT OF DILUENT CONCENTRATION ON PULSE HEIGHT

- A - Methanol Dilution Curve in Cell A DuMont K1190 tube
- B - Methyl Borate Dilution Curve in Cell B E.M.I. tube
- C - Methyl Borate Dilution Curve in Cell B DuMont K1190 tube

(b) Cells

Two cells used in the actual dating measurements in this work are illustrated in Figure 2. Cell A was designed for use on the one inch diameter semi-transparent cathode end-window photomultiplier tube (Dumont K1190 No. 7923), and was employed in measurements on labelled methanol. Capacity of the cell was 20 millilitres and a capillary tube sealed to the inner member of a 10/30 ground glass standard taper joint permitted the bubbling of dry oxygen-free nitrogen through the solution. A thin lucite jacket was fitted around the cell in such a manner that a small space existed between the side and top of the cell and jacket. Finely powdered magnesium oxide packed into this space provided an excellent reflector. One inch lengths of "tygon" tubing, of proper diameter, attached to each of the openings in the bubbler head facilitated connection of the cell to the bubbling line.

Cell B was originally designed for testing various liquid scintillator solutions on the $1\frac{1}{2}$ inch EMI photomultiplier tube. However, when it was discovered that methyl borate solutions in cell B gave a higher fluorescence efficiency (see page 33) when measured with the 1 inch Dumont K1190 tube than did similar solutions in cell A, its usefulness for actual counting measurements with labelled methyl borate was established. The design of cell B was basically the same as that of cell A; a capillary was provided for bubbling nitrogen through the solution, and magnesium oxide, encased outside the cell in a thin lucite jacket, served as the reflector. Chief difference of cell B was its greater capacity 25 millilitres and larger diameter $1\frac{1}{2}$ inches. A lucite adaptor assured proper and secure seating of the cell on the one inch phototube.

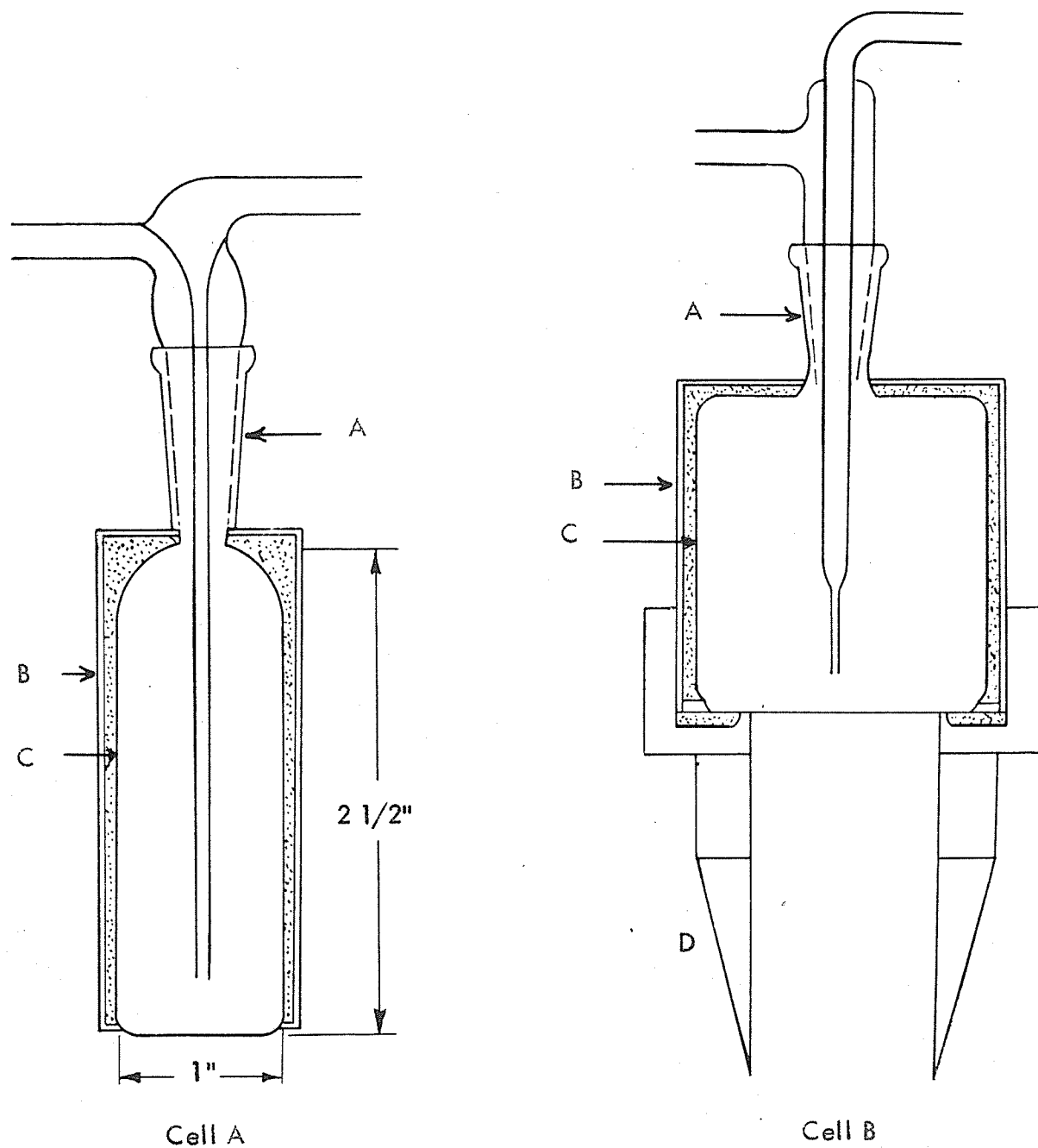


FIG. 2 LIQUID SCINTILLATOR CELLS

- A - 10/30 Joint
- B - Plastic Sleeve
- C - MgO Reflector
- D - Adaptor

(c) Shielding and electronic circuitry

A schematic diagram of the apparatus and shielding set up for low level counting by the Physics Department at the University of Manitoba is given in Figure 3. Detailed descriptions of the associated electronic circuitry have been published and are readily available. (39, 46) Figure 4 illustrates the simplicity of arrangement of counting equipment and shielding, one of the attractive features of the liquid scintillation counter in C^{14} dating.

To reduce the background counting rate to a minimum a large cylindrical shield having a wall thickness of 5 inches of lead and $1\frac{1}{2}$ inches of mercury was constructed. A cathode follower which served as a preamplifier for the pulses from the photomultiplier was attached to the base inside the shield. The photomultiplier tube, a specially selected Dumont K1190 of one inch cathode diameter, with the scintillator cell and adaptor mounted on it was plugged into the cathode follower and the mercury shield in the form of an inverted cup lowered over it.

In addition the entire apparatus was enclosed in a copper mesh cage 7 x 7 x 5 feet to eliminate high frequency interference arising from electrical fixtures, etc.

Pulses from the photomultiplier are passed by the cathode follower to a high gain (X 40,000 Radiation Instruments Co. Model 107-P) low noise non-overloading amplifier, then to a differential discriminator and finally are recorded on a decade scaler (Atomic Instruments Model 7). An Esterline-Angus pen recorder which indicated ticks for every 100 counts on the scaler provided a convenient counting rate versus time chart. Periods of electronic instability indicated by an extremely large number

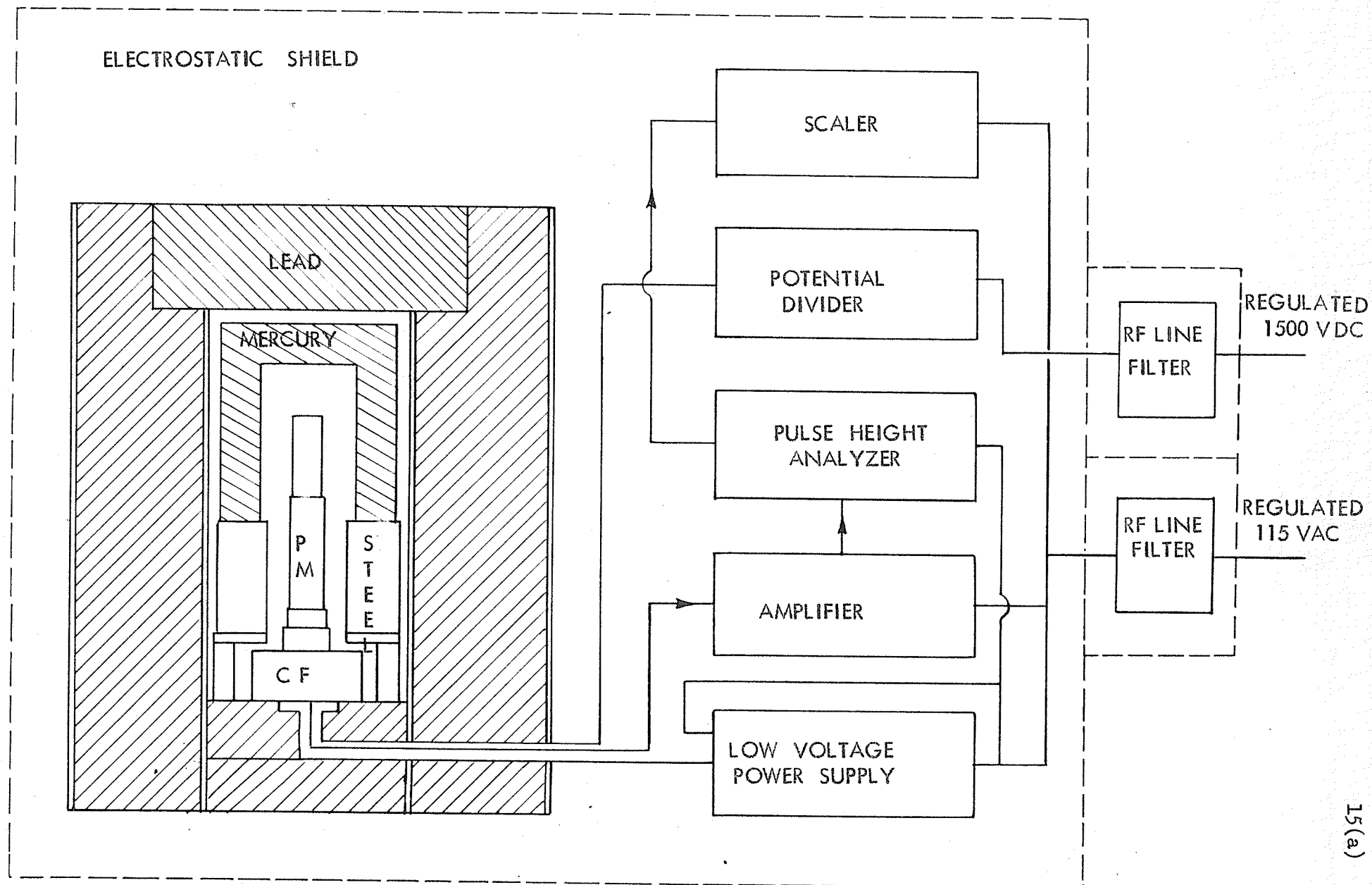
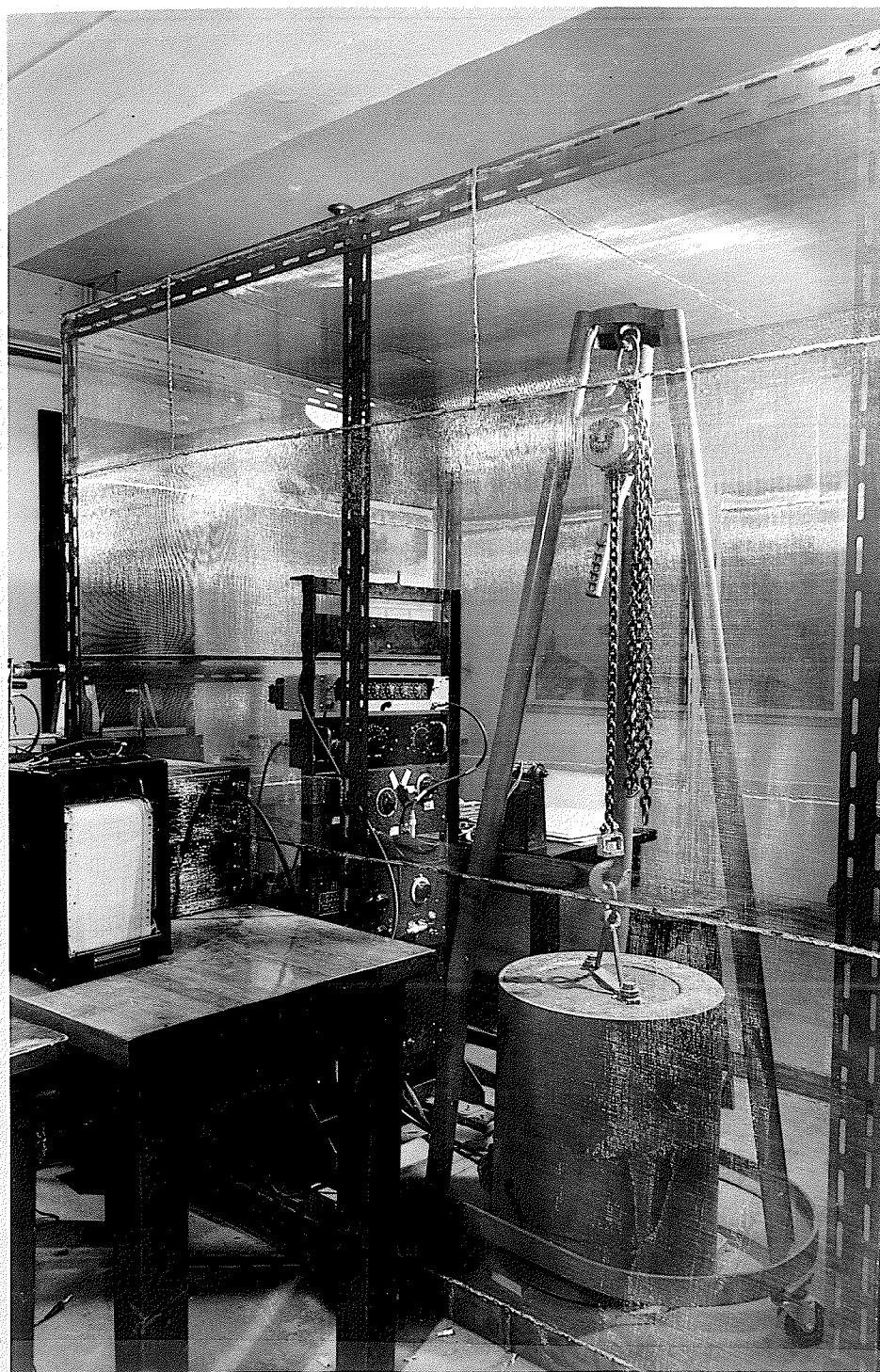


FIG. 3 BLOCK DIAGRAM OF COUNTING APPARATUS AND SHIELDING

FIG. 4

ARRANGEMENT
OF COUNTING APPARATUS



of closely-spaced ticks were eliminated from the overall record. Use of the differential discriminator makes it possible to select only those pulses in the range of energies corresponding to the beta energy spectrum for C^{14} . This factor helps reduce the background counting rate since pulses due to high energy cosmic rays are not recorded.

EXPERIMENTAL

Since the preparation of a carbonaceous sample for measurement of its activity consists of several well defined steps the description of the individual procedures involved will be carried out under the following main headings:

A. Preparation of Samples for Synthesis

(a) Preliminary treatment of sample

(b) Combustion

(i) Materials

(ii) Combustion procedures

B. Chemical Synthesis

(a) Synthesis of methanol

(i) Materials

(ii) Procedures

(b) Synthesis of methyl borate

(i) Materials

(ii) Procedures

C. Preparation of Solutions for Measurements

(a) Basic liquid scintillator solutions

(i) Materials

(ii) Technique

(b) Treatment of solutions containing diluents

A. Preparation of Samples for Synthesis

(a) Preliminary treatment of sample

The importance of careful examination and separation of the material to be dated has been established in Libby's monograph.⁽³⁵⁾ Data-ability of various materials, techniques of preparation of samples and possibilities of errors have been discussed by Libby and others. A review is given by Kohman and Saito.⁽³²⁾ Wood and peat were generally found to be suitable materials.

The samples received were carefully removed from their containers. Outside layers of the wood samples were then scraped clean with a sharp knife in order to dislodge any dirt and foreign matter present on the surface. Soaking of the wood in 3N HCl for approximately six to twelve hours, depending on the amount of effervescence noted, served to remove any carbonates deposited in the cracks of the wood. Following the acid soaking, the wood was washed with large amounts of freshly boiled distilled water and allowed to dry. Samples treated in this manner were then stored in glass jars under a N_2 atmosphere.

For peat samples the procedure was slightly different. Since the samples invariably contained a much higher percentage of inorganic matter, the period of acid soaking was extended to forty-eight hours, followed by a filtration and washing with freshly boiled distilled water. Storage of the peat samples was similar to that of the wood.

In preparing methanol of contemporary origin, Manitoba beet sugar, known to be at most a year old, and of high purity, was utilized in the combustion step. CO_2 of petrochemical origin was obtained by combusting U.S.P. benzoic acid prepared from toluene known to be of petrochemical origin.

(b) Combustion of sample

(i) Materials

In the synthesis of a compound to be employed in the liquid scintillation method of radiocarbon dating one must take special care in avoiding as much as possible any materials which could conceivably contaminate the final product.

Barium hydroxide

The barium hydroxide, used in preparing solutions for the absorption of the carbon dioxide generated during a combustion, was of reagent grade. It was obtained, in the form of the octahydrate, from the J.T. Baker Company, Toronto, Ontario.

Perchloric acid

Perchloric acid used to generate the carbon dioxide from the barium carbonate was of reagent grade and was obtained from the J.T. Baker Company, Toronto, Ontario. Thirty per cent perchloric acid was made by mixing equal parts of distilled water and acid.

(ii) Combustion procedures

Combustion of carbonaceous samples was carried out on a macro scale, a procedure similar to that of Sobering⁽⁴³⁾ being followed with several modifications.

For samples of high carbon and low inorganic content, approximately 100 to 150 grams of the carbonaceous material were combusted. Large inorganic content resulted in proportionate increases in amount of material combusted. Peat samples, usually consisting chiefly of inorganic components, were combusted in amounts up to 300 grams.

Oxidation of the carbonaceous material to carbon dioxide was carried out in a 20 millimeter i.d. and 100 centimeter long Vycor tube packed for eighty centimeters of its length with fresh wire form copper oxide free of any contaminating CO_2 . Heat was supplied by a three element macro furnace. Oxygen, used for the combustion, was drawn from a cylinder and passed through a drying train consisting of one sulphuric acid bubbler, one calcium chloride tube, and two ascarite tubes which served to remove

traces of water and carbon dioxide respectively.

A temperature of 500 - 650°C was maintained in the Vycor tube during the combustion by two of the elements; the temperature of the third was adjusted in such a manner as to assure an even combustion of the sample, eliminating "flash-backs" and minor explosions. Plugs of silver wool, inserted in the tube removed sulphur compounds formed during the combustion of wood and peat.

The combustion gases were bubbled successively through two five litre flasks containing aqueous barium hydroxide. Solutions of barium hydroxide were made up by dissolving $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ in freshly boiled distilled water until the saturation point was reached. They were allowed to stand overnight, thus settling any carbonates to the bottom of the flask. Transference, under nitrogen pressure, through a sintered-glass filter stick to absorption flasks previously well flushed with nitrogen enabled one to obtain perfectly clear solutions for the absorption of the carbon dioxide. Agitation of the solution in the first flask by means of a "Trubore" ground glass stirrer hastened absorption of the carbon dioxide by the Ba(OH)_2 considerably. The second flask served as a safety trap, preventing back up of the atmosphere into the first flask. It was found that insertion of a trap between the combustion tube and the first flask helped to eliminate mechanical carry-over of combustion particles into the flask.

Following completion of the combustion, the barium carbonate in the first flask was allowed to settle overnight. The supernatant barium hydroxide solution was then neutralized with 3N HCl until the pink color due to several drops of phenolphthalein indicator added vanished. A.

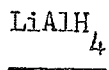
vigorous shaking of the contents usually made the pink color reappear, indicating that slight amounts of barium hydroxide were trapped in the precipitate. Further addition of HCl neutralized this barium hydroxide. Several such shakings and treatments with HCl were necessary to completely remove traces of barium hydroxide. This procedure was quite important since exposure of the precipitated barium carbonate to the atmosphere was necessitated during the filtration step.

The contents of the absorption flask were then filtered with suction through a 15 centimeter Buchner funnel and the BaCO_3 , following several washings with carbon dioxide-free distilled water, was dried in an oven at 110-120°C. Storage of the dried barium carbonate under nitrogen, in tightly stoppered glass bottles served to prevent the exchange of atmospheric carbon dioxide with the carbonate. (10)

B. Chemical Synthesis

(a) Synthesis of methanol

(i) Materials



For the methanol synthesis, the lithium aluminum hydride employed in the reduction step was obtained from the Metal Hydride Corporation, 12 Congress Street, Beverly, Mass. Cox et al⁽¹²⁾ had reported the presence of adsorbed carbon dioxide on the hydride used by them in the reduction step. Since the presence of any carbon dioxide adsorbed on the surface of the hydride would greatly interfere in any age determinations with methanol or methyl borate, it was decided to investigate the degree of contamination of the hydride employed.

LiAlH_4 obtained from the manufacturer was of commercial grade and was packaged in tin containers, under a nitrogen atmosphere, with a minimum of contact with the atmosphere. (7) It was used without further purification since the following tests showed the presence of any adsorbed CO_2 to be negligible.

3.3 grams of lithium aluminum hydride, taken directly from the container were placed in an eight inch test tube previously flushed with N_2 . 110 millilitres of a solution of equal parts of reagent grade dioxane and water were added drop by drop to the hydride. The resulting gases were then bubbled through a perfectly clear solution of $\text{Ba}(\text{OH})_2$ which had been filtered through a sintered-glass filter stick under nitrogen. The presence of even trace amounts of CO_2 absorbed on the hydride would be detected by the formation of BaCO_3 .

In addition to the preceding test, a blank synthesis was also run. Presence of methanol as the product following the decomposition and alcoholysis step would ascertain whether the LiAlH_4 was contaminated to any serious extent with adsorbed CO_2 .

.74 moles of LiAlH_4 was dissolved in 500 millilitres of diethyl carbitol in a three-necked three litre flask under a nitrogen atmosphere. Decomposition of the hydride was effected by adding 550 millilitres of n-butyl carbitol slowly to the solution, keeping the reaction flask cooled in an ice-salt mixture. The contents of the flask were then subjected to a vacuum distillation at a pressure of 10 m.m. and a temperature of 30°C . Since no distillate was collected in the dry-ice traps, the presence of adsorbed CO_2 on the original hydride was shown to be below the limits of error inherent in radiocarbon measurements.

Finally a sample of "old" methanol was synthesized from CO_2 prepared by the combustion of "old" benzoic acid. If any CO_2 was adsorbed on the hydride it would presumably result from contact of the hydride with the atmosphere. Consequently, if the counting rate due to the "old" methanol synthesized was higher than the background counting rate of the liquid scintillator employed, the possibility of contamination with adsorbed CO_2 would be quite serious. Actually, the counting rate of the synthetic "old" methanol was indistinguishable from that of the background.

Diethyl Carbitol (1-ethoxy-2-(B-ethoxyethoxy ethane)

Used as the solvent for the LiAlH_4 in the methanol synthesis; it was obtained from the Carbide and Carbon Chemicals, Toronto, Ontario, and Eastman Chemicals. (The use of various solvents and alcoholyzing agents had been investigated in detail by Cox et al). Because it is relatively non-volatile, and because it is easily available in large quantities without too great an expense the diethyl carbitol was chosen as the solvent. The diethyl carbitol as purchased from the manufacturer is listed as being of 99% purity⁽¹¹⁾ with a boiling point of 188.9°C and $n_D = 1.4098$.

Purification of the diethyl carbitol consisted of a drying with anhydrous CaCl_2 followed by distillation through a 75 plate column. The fraction boiling at a pressure of 5 m.m. and temperature range of $45^\circ - 46^\circ\text{C}$ was collected. There was, however, a slight evolution of gas when the LiAlH_4 was dissolved in the purified diethyl carbitol. This could be explained by traces of water not removed, and possibly traces of high boiling alcohols.

n-Butyl Carbitol (diethylene glycol monobutyl ether; 2-(B-butoxyethoxy ethanol)

The n-butyl carbitol used as the hydrolysis agent in the second

step of the methanol synthesis, was also obtained from two sources, Carbide and Carbon Chemicals, Toronto, Ontario, and Fisher Scientific, Toronto, Ontario, and is listed as possessing a purity in the region of 96%.⁽¹¹⁾ No significant difference in yields was noticed in using carbitol from either of the sources. Choice of the n-butyl carbitol as the alcoholysis agent rested on its high boiling point, and because it could be readily obtained at low cost.

Since the presence of measurable amounts of water in n-butyl carbitol would contaminate the methanol, purification of the n-butyl carbitol consisted of a drying with anhydrous CaSO_4 followed by distillation through the 75 plate column. The fraction boiling at a pressure of 3 m.m. and a temperature of 80°C was collected.

(ii) Procedures

Apparatus employed in the reduction step is illustrated in Figure 5. The barium carbonate was placed in the 500 c.c. Erlenmeyer flask B and 30% perchloric acid in the 300 c.c. dropping funnel A. Use of the Erlenmeyer enables spreading of the barium carbonate in as shallow a pile as possible, facilitating contact with the perchloric acid.⁽¹⁰⁾

The hydride-diethyl carbitol was transferred, under a nitrogen atmosphere, through a sintered-glass filter stick, into the three-necked, five litre capacity reaction flask C. The pressure in the system during the reaction could be measured by the open-end mercury manometer. Before each synthesis the entire system was thoroughly flushed with nitrogen and tested for any leaks to the atmosphere. All ground glass connections were lubricated with Dow-Corning silicone grease. This was found to give an air-tight seal for long periods. Rubber to glass connections were coated

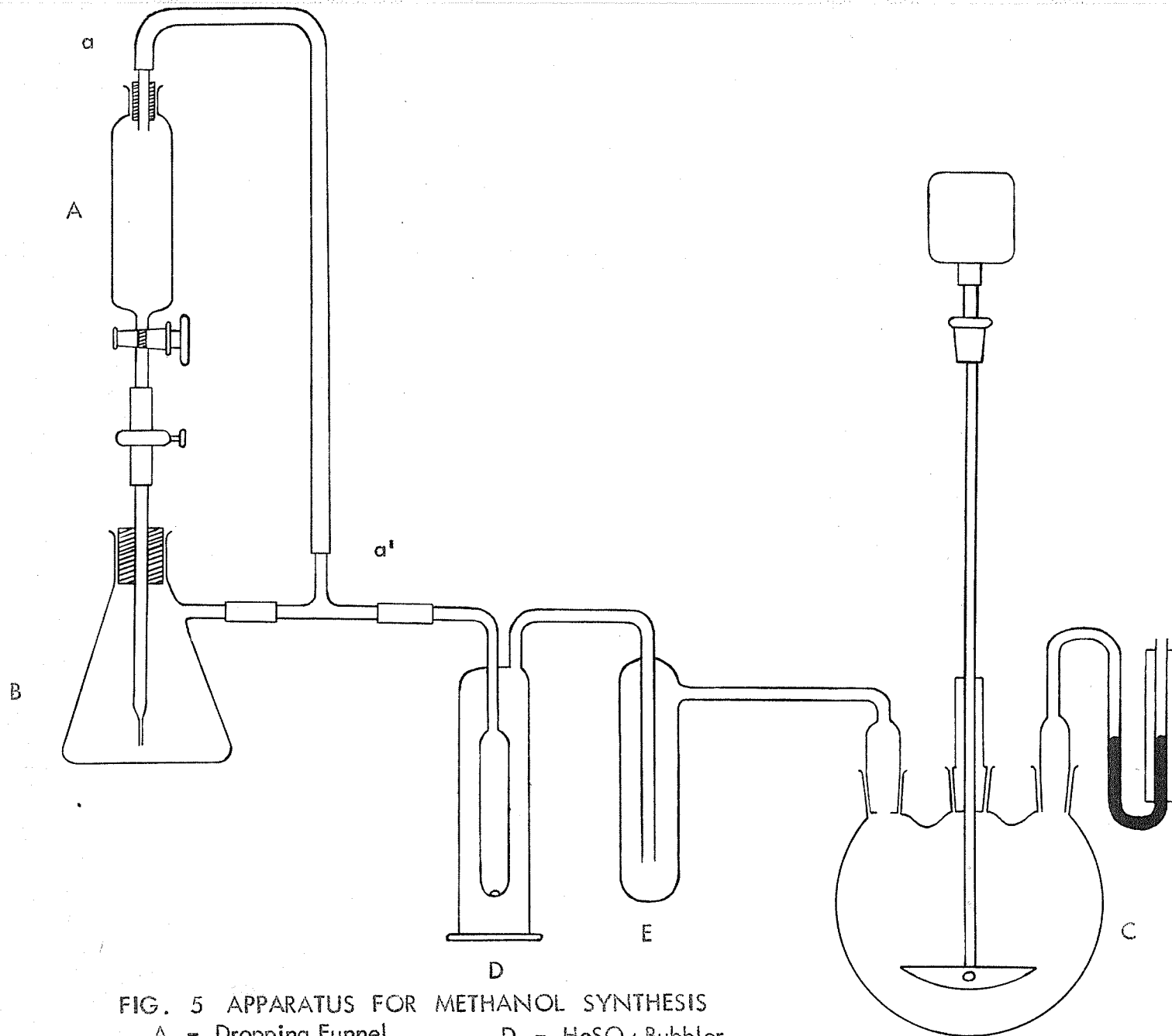


FIG. 5 APPARATUS FOR METHANOL SYNTHESIS

A - Dropping Funnel	D - H_2SO_4 Bubbler
B - Erlenmeyer Flask	E - Water Vapor Trap
C - 5-Litre Reaction Vessel	aa' Rubber Tubing

with "Seal-it". The sulphuric acid bubbler D, and the trap E, immersed in a dry-ice-acetone mixture, removed any water vapor carried over with the CO_2 generated in the Erlenmeyer.

Agitation of the contents of the reaction flask during the reduction and alcoholysis steps was provided by means of a "Trubore" stirrer run by a constant torque stirring motor. Cooling of the reaction flask itself in an ice-salt mixture during the reduction step was found to increase the rate of absorption of the CO_2 by the hydride considerably.

In a typical reaction, (St. Pierre wood) .602 moles (118.6 grams) of BaCO_3 was placed in the Erlenmeyer and 195 millilitres of 30% perchloric acid in the dropping funnel. The manometer was then removed and the hydride-diethyl carbitol solution containing 1 mole (38 grams) of LiAlH_4 dissolved in 1300 millilitres of diethyl carbitol transferred to the reaction flask while a flow of nitrogen was maintained through the system. The manometer was replaced and the CO_2 generated by slowly dropping the perchloric acid onto the barium carbonate. By means of the rubber tubing a ¹ a pressure balance was maintained in the system ensuring a smooth flow of the acid, whose rate was adjusted by means of a screw clamp. When the pressure in the system was 2 - 3 centimetres higher than atmospheric pressure, the manometer was loosened slightly and the nitrogen trapped in the flask was flushed out by the carbon dioxide. The manometer was then replaced and the stirrer turned on. Absorption of the gas by the hydride solution started immediately. The carbon dioxide was generated at such a rate as to have the pressure in the system several centimeters higher than atmospheric pressure, eliminating possibilities of contamination, should any leak develop during the course of the reaction. When the absorption of

carbon dioxide generated by the barium carbonate was completed, usually within two to three hours, the tubing at "a" was connected through an ascarite tube to a nitrogen cylinder. Nitrogen was then bubbled into the system until all traces of carbon dioxide were absorbed by the solution. With a flow of nitrogen maintained through the system, the manometer was replaced by a 500 c.c. dropping funnel equipped with an outlet through which the nitrogen could escape. A trap immersed in dry-ice-acetone was connected to this outlet by means of rubber tubing. 475 millilitres of n-butyl carbitol were then placed in the dropping funnel. The flow of nitrogen was adjusted to 3 - 4 bubbles per second and the carbitol was allowed to drop very slowly into the reaction flask which was cooled in ice-salt. Caution was exercised in this step for the large volume of hydrogen evolved during the decomposition step could be ignited quite easily if the rate of decomposition is too rapid. A safety shield was installed in the event that any explosion should occur. The hydrogen was flushed out of the flask through the trap and into the fume hood by the nitrogen. Approximately 300 millilitres of n-butyl carbitol were necessary to decompose the excess hydride. Following the decomposition, a further 1435 millilitres of n-butyl carbitol were added to hydrolyze the complex salt and yield the methanol.

Distillation of the methanol from the reaction flask was accomplished in the following manner. A nitrogen bleed was inserted in one neck of the reaction flask; a thermometer placed in the other. The stirrer was removed and in its position were connected two traps in series, immersed in Dewars containing dry-ice-acetone mixture. The second trap was connected through a simple manometer to a vacuum pump. A pressure

of 2 millimeters was maintained during the distillation with the aid of the bleed, and the temperature was raised to 27°C by means of a heating mantle. When about 40 millilitres of distillate had been collected in the first trap, the distillation was discontinued, and a refractive index taken of the crude methanol. It was found to be 1.3710. The distillate was transferred to a 100 c.c. flask and kept for subsequent purification. Further vacuum distillation of the methanol from the reaction flask was attempted but the refractive index of the distillate collected, 1.3980, indicated that it was chiefly diethyl carbitol. This portion was added to the previous distillate.

Purification of the crude methanol distillate consisted of a distillation through a semi-micro fractionating column. This column was similar to the one used in the distillation of the toluene in the toluene synthesis.⁽⁴³⁾ It consisted of a glass tube 9 millimeters in diameter and 40 centimetres long filled with glass helices and equipped with a reflux-head. The tubing was insulated with cotton batting held in place by 4 centimetres diameter glass tube wrapped with a heating tape. Thus the temperature of the distilling column could be maintained at the same temperature as that of the liquid being distilled. An efficiency of 8 theoretical plates could be obtained with it.

The methanol was distilled through this column and the fraction boiling in the range of $64^{\circ} - 65^{\circ}\text{C}$ and pressure of 748 mm. was collected in a flask immersed in a mixture of dry-ice-acetone. A calcium chloride tube attached to the outlet of the system prevented any atmospheric water vapor from condensing in the receiving flask. The temperature stayed constant in this range and when all of the methanol had distilled over it

dropped. The fact that the temperature did not go above 65°C indicates that the product was extremely pure and was free of contaminants such as ethanol and water. Since methanol does not form any azeotrope with water, it may be separated completely from water by fractional distillation.⁽⁵¹⁾

The refractive index of the redistilled methanol determined on an Abbe refractometer was 1.3309. A yield of 14.25 grams or 75% calculated on the basis of CO₂ generated was obtained. A refractive index of 1.4079 was obtained for the residue left in the distilling flask, indicating that the chief impurity present in the crude methanol was diethyl carbitol. Data for the syntheses carried out in the investigation are listed in Table II.

(b) Synthesis of methyl borate

(i) Materials

Boric Oxide

Anhydrous boric oxide used in the syntheses was of reagent grade and was obtained from the J.T. Baker Co. Toronto, Ontario. It was employed without further purification.

Lithium Chloride

Anhydrous lithium chloride obtained from the J.T. Baker Co. of Toronto, Ontario was of reagent grade. Except for drying in an oven at 110°C to remove traces of moisture, the lithium chloride was utilized without further purification.

(ii) Procedures

Apparatus used in the methyl borate synthesis is illustrated in Figure 6. Since the actual syntheses were on a much smaller scale than those of Schlesinger et al modifications of Schlesinger's techniques were

necessitated.

A 100 millilitre one-necked flask A with an attached side arm B, through which finely powdered boric oxide could be added, served as the reaction vessel. To the flask was attached a fractional distillation column consisting of a glass tube nine millimetres in diameter and sixteen centimetres long filled three quarters of its length with glass helices. The column was encased in a five centimetre diameter glass tube plugged with cotton wool. A reflux head was fitted to the top of this column.

A sixty millilitre cone-shaped flask, protected from the atmosphere by means of a calcium chloride tube, served as the receiving flask. Before each synthesis the entire system was flushed thoroughly with nitrogen.

In a typical synthesis of methyl borate 18.80 grams (.59 moles) of methanol prepared from the Missinaibi River peat sample were placed in the reaction vessel. 13.72 grams of finely powdered boric anhydride were then weighed out and separated into four portions. Each portion was added separately through the side arm of the reaction flask to the methanol. Following each addition, the contents of the reaction vessel were refluxed gently. Upon completion of the addition the reaction mixture was heated for a further two to three hours. The contents were then distilled through the column and collected in the receiving flask which was immersed in a Dewar flask containing dry ice. The temperature range of the distillate collected was $53 - 55^{\circ}\text{C}$ indicating that it consisted chiefly of the methanol-methyl borate azeotrope whose boiling point is 54.6°C .⁽⁴²⁾ In most of the syntheses a hard white solid remained in the reaction vessel. The residual material was presumably methyl metaborate.⁽⁴²⁾

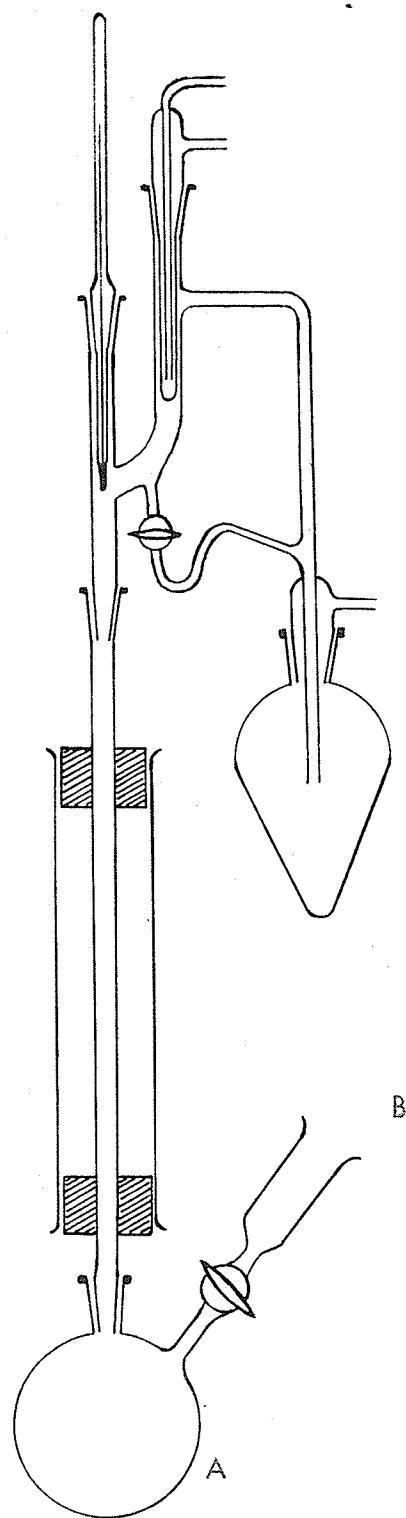


FIG. 6 APPARATUS FOR METHYL BORATE SYNTHESIS

- A - Reaction Flask
- B - Side Arm for Boric Oxide Addition

After disconnecting the receiving flask from the system, 4.2 grams of anhydrous lithium chloride, which had been further dried overnight in an oven at 110°C , were rapidly added to the distillate. The flask was then stoppered and vigorously shaken until two liquid layers were formed. After the excess lithium chloride had settled to the bottom of the conical flask, the top layer consisting of almost pure methyl borate was separated from the bottom layer composed of methanol and lithium chloride by means of a micro separatory funnel.

Purification of the methyl borate consisted of two distillations through the semi-micro fractional distillation column described in the methanol synthesis. The entire system was flushed with nitrogen and the receiving tube, which was immersed in dry ice, was protected from the atmosphere by a calcium chloride tube.

Two separate fractions boiling in the ranges $53 - 55^{\circ}\text{C}$ and $67 - 68.5^{\circ}\text{C}$ at atmospheric pressure were observed. The first fraction amounting to 4 millilitres was in all probability part of the methanol-methyl borate azeotrope not separated by the lithium chloride; the boiling point of the second indicated that it was methyl borate.

Further purification was accomplished by the addition of anhydrous lithium chloride to the once distilled methyl borate followed by a second distillation through the fractionating column. A product boiling in the range $67.5 - 68.5^{\circ}\text{C}$ was collected indicating that separation of the methyl borate from the methyl alcohol was complete. Because of the rapid decomposition of methyl borate upon exposure to the moist atmosphere no accurate measure of the refractive index was possible.

The yield of methyl borate, calculated on the basis of boron

converted to borate, was 71%. Data and yields for various samples of methyl borate synthesized are listed in Table III. Recovery of the methanol from the lower layer was achieved by a simple one plate distillation. The boiling point range of the distillate was $63.5^{\circ}\text{C} - 65^{\circ}\text{C}$.

C. Preparation of Solutions for Measurement

(a) Basic liquid scintillator solutions

(i) Materials

Xylene

Reagent grade xylene was employed as the solvent in all the basic scintillator solutions used for methanol and methyl borate dating measurements. It was obtained from the J.T. Baker Co., Toronto, Ontario, in 500 c.c. lots; the boiling point range was listed as $139.9 - 140^{\circ}\text{C}$ and $n_D^{20} = 1.4929$. No further purification of the xylene was attempted since an earlier work⁽⁴³⁾ indicated that no significant increase in pulse height efficiency was obtained after additional distillation.

p-Terphenyl (TP) (M. P. 213°C)

The p-terphenyl used as the primary solute in the basic scintillator solution employed in methanol measurements, was supplied by the Arapahoe Chemical Co., Boulder, Colorado. It was listed as being of scintillation grade and no further purification was deemed necessary.

1, 4-di-(2-(5 phenyloxazolyl)) - benzene (POPOP) (M.P. = $158 - 159^{\circ}\text{C}$)

Used as the secondary solute in the scintillator solution composed of p-terphenyl and xylene was obtained from the Pilot Chemical Co., Waltham, Mass. It was used without any additional purification.

2-phenyl-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) (M.P. = 167 - 169°C)

Source of the PBD was also the Arapahoe Chemical Co., Boulder, Colorado. This primary solute was of scintillation grade purity. Further purification by recrystallization from toluene⁽³¹⁾ did not alter the characteristics of the scintillator solution.

Naphthalene (M.P. = 80.22°C)

Naphthalene which serves as a secondary solvent in the basic scintillator solution used in methyl borate measurements, was obtained from the Fisher Scientific Co., Toronto, Ontario. It was listed as being recrystallized twice from alcohol and consequently no further purification was attempted.

(ii) Technique

Liquid scintillator solutions were made up in sufficient quantities such that all measurements of both the background and sample counting rates could be carried out using aliquot portion of the same stock solution. This procedure was carried out in both the methanol and methyl borate methods and eliminated any errors which could conceivably arise if solutions were prepared with chemicals from different batches.

A basic scintillator solution, composed of 4 grams/litre terphenyl as the primary solute, .1 gram/litre 1,4-di-(2-(5 phenyloxazolyl)) - benzene (POPOP) as the secondary solute (wave-length shifter), and xylene, giving a fluorescence efficiency of 72% relative to anthracene after nitrogen bubbling was found suitable for use with methanol as diluent.

Curve A, Figure I was obtained using Cell A mounted on an E.M.I. 1½ inch photomultiplier tube; relative pulse heights were determined by reading the pulse height corresponding to an integral counting rate of

160 counts per minute and comparing with an anthracene crystal similarly mounted. A 2.5 μ c sample of C_s^{137} emitting .255 Mev γ rays served as the source. Discussion of the choice of a liquid scintillator containing 30 per cent by weight of methanol for dating measurements is given on page 44.

In the methyl borate method the basic liquid scintillator solution used was composed of 3 grams/litre, 2-phenyl-5-(4-biphenyl)-1, 3, 4-oxadiazole (PBD) as the primary solute, 70 grams/litre naphthalene as secondary solvent and xylene. A pulse height efficiency of 76% relative to anthracene was obtained after bubbling with dry oxygen-free nitrogen. Further increase in concentration of primary solute to 8 grams/litre PBD raised the fluorescence efficiency only slightly.

The dilution curve B, Figure I for methyl borate was obtained with cell B mounted on the $1\frac{1}{2}$ inch E.M.I. photomultiplier tube in a similar manner as for methanol.

Tests of the above basic liquid phosphor using cell A, on a one inch Dumont K1190 photomultiplier tube showed that the relative pulse height efficiency was considerably lower than the value observed with cell B on the E.M.I. tube. In addition, it was found that the fluorescence efficiency of this basic solution, obtained with cell B mounted on the Dumont K1190 tube by means of the adaptor was higher by 10 per cent than that obtained with cell A. Therefore, a methyl borate dilution curve C, Figure I for cell B on this tube was determined. It should be remarked that no such anomalous behaviour was observed when the dilution curve for methanol was repeated using cells A and B on both photomultiplier tubes. Cell B was employed with the K1190 tube for actual dating measurements on labelled

methyl borate samples.

(b) Treatment of solutions containing diluents

To illustrate the procedures involved in setting up a synthesized methyl borate sample for the measurement of its activity the following description suffices.

A cell of type B was thoroughly cleaned, dried and flushed with nitrogen. To it were transferred 23.96 grams of solution composed of 7.52 grams (31.4% by weight) of methyl borate synthesized from the St. Pierre S-5 wood sample and 16.44 grams of stock liquid scintillator (70 grams/litre naphthalene, 3 grams/litre PBD and xylene). The capillary bubbler, with a small dab of silicone grease on the ground glass joint, was then fitted to the cell, and the arrangement attached to the nitrogen drying train by means of the short piece of "tygon" tubing on the bubbling arm. Nitrogen taken from a cylinder was passed through a drying train consisting of one pyrogallol bubbler to remove oxygen, 4 "U" type drying tubes, two of which were filled with anhydrous CaSO_4 and the other two with silica gel, and one xylene bubbler serving as a saturator. Bubbling at the rate of 1 - 2 bubbles per second was continued for a period of twenty-five minutes. A special trap connected to the outlet tubing of the bubbler and immersed in an ice-salt mixture (for methanol an acetone-dry-ice mixture) trapped any of the vapors carried out of the cell by the nitrogen stream. The weight of the liquid collected in the trap never amounted to more than .09 grams and corrections applied to the solution in the cell were, therefore, almost negligible. Upon completion of the bubbling the "tygon" connections on the bubblers were pinched tight with Hoffman screw clamps. All "tygon"-glass connections were then liberally coated with Fisher "Seal-It", insuring

against any leakage of the atmosphere into the cell. After fitting the adaptor to the bottom of the cell the sample was ready for measurement.

Except for the use of Cell A and a different basic scintillator solution, the steps followed in the methanol measurement were identical with the above.

Samples were stored in 50 c.c. screw-cap glass bottles previously flushed with nitrogen. A thin aluminum foil sealed over the cap and upper part of the bottle with paraffin prevented evaporation of contents.

DATA AND RESULTS

In line with the development of the experimental section the results are presented in the following order.

- A. Documentation of Samples Investigated
- B. Data and Yields for the Methanol and Methyl Borate Syntheses
- C. Results of Counting Measurements
 - (a) Range of the methanol and methyl borate methods
 - (b) Ages of samples investigated

A. Documentation of Samples Investigated

A complete list of the samples investigated along with their origin and description is given in Table I. Both methanol and methyl borate were synthesized from beet sugar and were used to establish the activity of contemporary radiocarbon as measured by the liquid scintillation counter. "Old" methanol and methyl borate were prepared from benzoic acid of petrochemical origin.

Documentation of the samples was provided by the collector in each case. Several additional points concerning these samples may be added. Interest in the wood sample S-4 collected by Prof. Lougee stems from a growing body of data which indicates the contemporaneity of post-glacial upthrusts of glacial sea-shores on either side of the North Atlantic Ocean. This sample found on the bank of the St. Lawrence River was thought to be part of such an upthrust and any dating measurements on it would be significant. A similar situation was presented in the wood sample S-3

collected in the Bay of Fundy.

The two samples S-6 and S-7 submitted by O.L. Hughes of the Geological Survey of Canada were thought to be remnants of a glacial retreat in northern Ontario and were collected from the same location.

Sample S-5 St. Pierre Wood was previously dated by three different groups using the solid-carbon and acetylene methods. These results were as follows.

L-190 A	11,050 \pm 400 years (possibility of contamination suggested by J. Lawrence Kulp) (solid carbon)
Y-242	20,300 \pm 4000 - 3000 years. Solid carbon method.
W-189	>40,000 years - dated by acetylene method in Washington.

An explanation for the serious differences in the three dates may be offered by the fact that the wood samples analysed were all part of a gross grab sample; the pieces of wood were generally too small to allow sampling of a single piece for all analyses.

Documentation on the wood sample S-8 collected from a farmer's well in Alberta was vague and details other than its origin were lacking.

TABLE I
Documentation of Samples Investigated

Sample Number	Nature of Sample	Locality	Description of Sample
S-1	Benzoic Acid		Prepared from toluene of petrochemical origin
S-2	Beet Sugar	Manitoba	Contemporary origin
S-4	Wood	Micmac terrace Baie St. Catherine, Quebec. Collector: Prof. Richard J. Lougee★	Several large pieces of coniferous wood, buried as driftwood; from 13 to 20 feet below the surface of the terrace
S-3	Wood	Drowned forest Bay of Fundy Amherst, Nova Scotia Collector: Prof. R. J. Lougee	One fork-shaped piece of wood or root from a stump situated at the drowned forest
S-5	Wood	St. Pierre Section, St. Pierre les Becquets, P.Q. Collector: N.R. Gadd★★	Several pieces of wood from peat layer No. 3
S-6	Wood	Field No. 24MB 24M - Missinaibi River - 6 miles above mouth of Soweska River, Northern Ontario, Date: August 18, 1954 Collector: O.L. Hughes★★★	One piece of wood from below peat horizon; wood at base 2.9' till.
S-8	Wood	Alberta, Collector: Prof. C.P. Gravenor University of Alberta	One piece of wood obtained from a farmer's well at a depth of 27 feet

★ Department of Geography, Clark University
 ★★ Geological Surveys of Canada
 ★★★ Geological Surveys of Canada

TABLE I
Documentation of Samples Investigated

Sample Number	Nature of Sample	Locality	Description of Sample
S-7	Peat	Field 24MB South bank of Missinaibi River about six miles above Soveska River, Northern Ontario Date: August 18, 1954 Collector: O.L. Hughes, Geological Surveys of Canada	Three blocks of peat obtained from the peat horizon
S-9	Wood	Obtained from the University of Saskatchewan	Two pieces of wood

B. Data and Yields for the Methanol and Methyl Borate Syntheses

Syntheses of methanol and methyl borate were carried out for each of the samples listed in Table I; the data and yields are listed in Table II and Table III respectively. Techniques identical to those described in the experimental section were employed.

An analysis of Table II reveals an interesting correlation between the yields of methanol and the concentration of the hydride-diethyl carbitol solutions. Although yields of methanol of over 80% have been reported (2,37) for syntheses on a micro scale, the first syntheses on a macro scale resulted in much lower yields, in the vicinity of 50 - 60%. However, when more dilute hydride-diethyl carbitol solutions were used in the absorption step, a significant increase in yields to over 70% was observed. The variation of overall yields with change in concentration of the hydride-diethyl carbitol solution is illustrated in Figure 8. From the data in Table II and Figure 8 it would appear that reduction of the carbon dioxide by the hydride in the most concentrated solutions, although complete, did not lead to the formation of a complex which would yield methanol upon alcoholysis. In one instance, addition of several millilitres of hydrochloric acid to a small portion of the residual mixture from a synthesis followed by distillation, resulted in the collection of several drops of a compound possessing an odor similar to formic acid. It may well be that the reduction of the carbon dioxide to a complex formate is more favored in concentrated hydride-carbitol solutions even though in all the syntheses a large excess of the hydride was employed to prevent such an occurrence.

Columns 7 and 8 of Table II list the physical constants of the synthesized methanol samples. The values agree very well with those re-

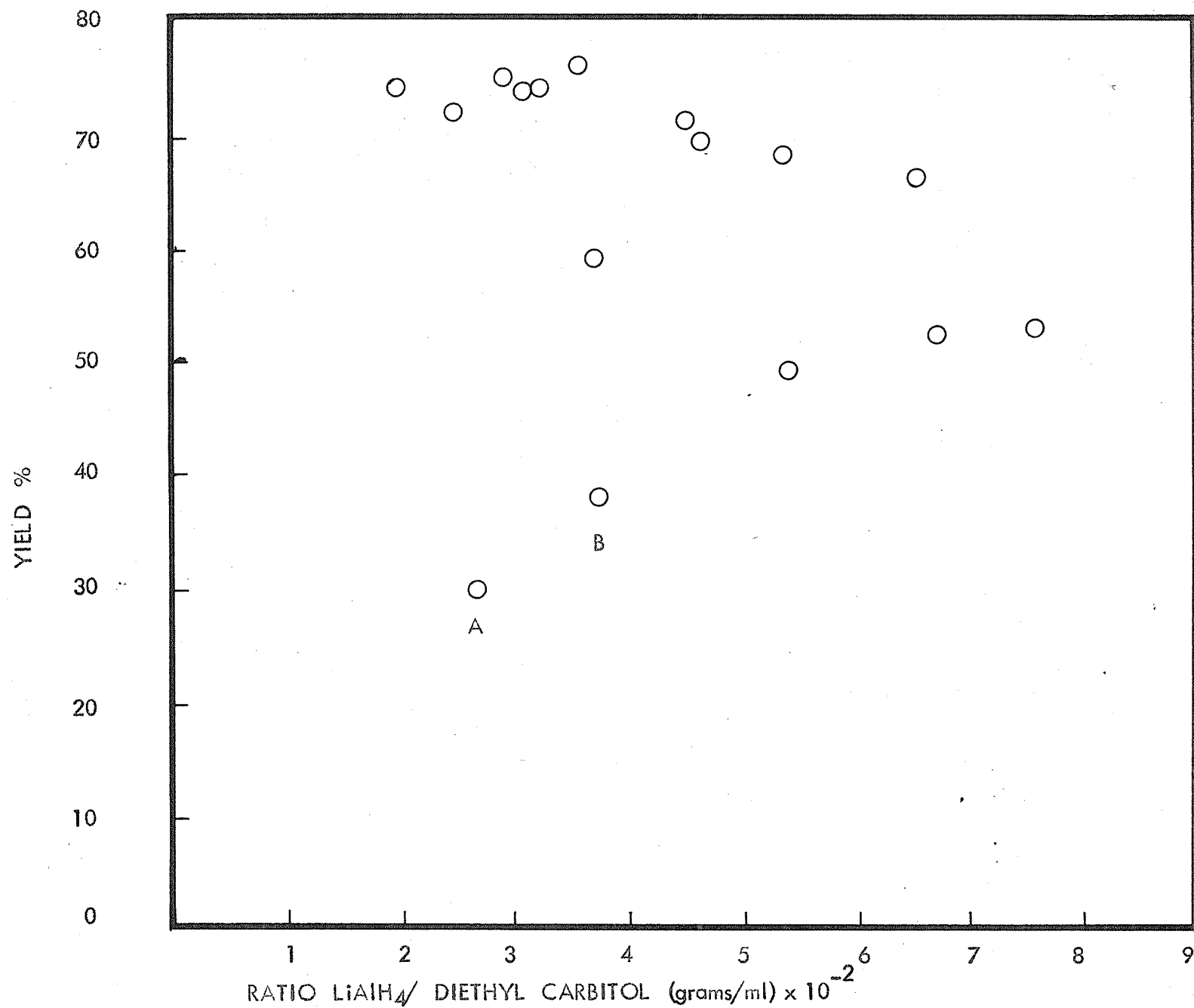


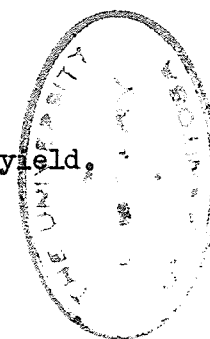
FIG. 8 VARIATION OF METHANOL YIELD WITH HYDRIDE CONCENTRATION

TABLE II
Data for Methanol Syntheses

Sample Number [*]	Moles of CO ₂	Moles of LiAlH ₄	Volume of Diethyl Carbitol (ml.)	Yield in (grams)	Yield in %	Boiling Point Range °C	Ref. Index n _D ^{20°}
S-1 (a)	.59	.84	850	7.36	38	64-64.8	1.3299
S-1 (b)	.62	.90	910	11.55	59	63-64.5	1.3307
S-2 (a)	.832	1.21	700	17.49	66	63.5-64	1.3298
S-2 (b)	.97	1.40	700	15.50	53	63.7-65	1.3301
S-2 (c)	1.05	1.24	700	17.16	52	62.5-64.5	1.3308
S-2 (d)	.99	1.65	2500	22.51	71	64.5-65	1.3318
S-3 (a)	.51	1.07	750	11.20	68	64.5-66	1.3309
S-3 (b)	.78	1.07	900	17.31	71	63.5-65	1.3301
S-3 (c)	.92	1.56	1300	20.30	69	63.5-65	1.3309
S-4	.63	.93	650	10.30	49	63.5-64	1.3299
S-5 (a)	.60	1.00	1300	14.25	75	64.5-66	1.3307
S-5 (b)	.71	1.12	1350	16.81	74	64.5-66	1.3303
S-6	.85	1.28	1350	20.67	76	63.5-65	1.3310
S-7	.94	1.50	1750	22.25	74	63.5-64	1.3299
S-8	.75	1.32	2500	18.80	74	63.5-64	1.3298
S-9 ^{**}	.91	1.54	2000	8.64	30	63.5-64	1.3310

* Nomenclature follows that used in Table I, page 38.

** Accidental loss of methanol resulted in a low overall yield.



corded in the literature B.P. = 64.509°C at 760 mm. and $n_D^{20} = 1.32863^{(49)}$.

Methyl borate samples were prepared from the purified methanol listed in Table II. Boiling points of the doubly-distilled products were in all cases very close to the value quoted by Schlesinger. Although the yields listed in column 5 were not as high as those reported by Schlesinger, there was no undue alarm since the mole ratio of boric oxide to methanol was so chosen as to allow maximum conversion of methanol to methyl borate.

A discussion of the possibility of isotopic fractionation in the foregoing syntheses will be given in the next section, Page 52 .

TABLE III

Data for Methyl Borate Syntheses

Sample Number	Weight of Boric Oxide (gms.)	Weight of Methanol (gms.)	Yield Methyl Borate (gms.)	Yield %
S-1 (a b) [*]	7.11	13.14	6.35	47
S-2 (a b c)	15.30	28.16 ^{**}	14.30	62
S-2 (d)	16.26	20.30	14.41	58.5
S-3 (b)	11.37	15.50	9.11	54
S-3 (c)	13.89	19.11	9.63	47
S-5 (a)	9.67	13.30	8.92	62
S-5 (b)	10.91	14.89	10.77	66
S-6	14.01	19.03	12.36	62
S-7	13.72	18.80	14.12	71
S-8	12.41	16.98	12.40	67

* S-1 (a) and S-1 (b) were combined in the methyl borate synthesis

** The mole ratio of methanol: boric oxide was 4:1 in this case.

C. Results of Counting Measurements

(a) Range of the methanol and methyl borate methods

An analysis of the problems which arise along with the results obtained in the counting of low level radiocarbon activities using both the methanol and methyl borate diluent methods will be given.

Considerations of the photomultiplier noise characteristics for liquid scintillators of various fluorescence efficiencies⁽³⁹⁾ indicate that the contribution of the photomultiplier tube noise to background counting rate is quite significant for liquid phosphors with low pulse height efficiencies. Indeed, use of liquid scintillators with a fluorescence efficiency lower than 35% relative to anthracene is impractical. Consequently bearing in mind Figure I Curve A showing the decrease in fluorescence efficiency with methanol concentration it is evident that the quantity of sample carbon introduced in the form of methanol into the liquid phosphor will be limited by the fluorescence efficiency of the resultant solution.

Further considering Figure I we see from curve B that quenching of fluorescence efficiency by addition of methyl borate is not nearly so severe as for methanol. An immediate consequence of this is that more labelled carbon atoms can be introduced into the scintillator than is possible with the methanol. Difficulties such as this are not encountered in the toluene method,⁽²⁵⁾ where the labelled atoms are a part of the molecules comprising the solvent component of the liquid phosphor.

In addition to the above conditions, a decision must be reached as to the optimum energy region in which to perform a count. The usefulness of the differential discrimination technique is at once evident

for it makes possible the counting of pulses in the energy region selected only.

To obtain the value for the counting rate of a contemporary methanol sample, a liquid scintillator weighing a total of 17 grams, giving a pulse height efficiency 35% relative to anthracene, and containing 4.97 grams of "modern" methanol was used. Total weight of "modern" carbon, part of which is C^{14} , was therefore 1.87 grams.

From considerations of Figure 7 showing the integral bias curves obtained for the methanol technique using the above solution⁽⁴⁶⁾, a count taken in the energy region of 40 kev to 135 kev would result in a background of 11.8 cpm. and a net sample carbon count of 14.2 cpm. Although the methanol method would thus be meaningful to 36,000 years, on the arbitrary basis that a net counting rate in excess of four times the standard deviation σ_B in the background counting rate is significant, and if one counts for 48 hours on both the unknown and the background, the rapid increase of the noise spectrum for the Dumont K1190 tube in this energy region creates a problem in realizing a completely stable background.

It may be noted that the standard deviation σ for any random process such as a radioactive disintegration is given by the following relation. $\sigma = \sqrt{n}$ where n is the total number of counts recorded in the interval of measurement.⁽²³⁾

To circumvent this difficulty a differential count was taken in the energy interval 45 kev to 135 kev yielding counting rates of 8.18 \pm 0.05 cpm and 7.39 \pm .08 cpm. for 48 hour counts on the background and net modern sample respectively. Pulse height efficiencies of both were adjusted

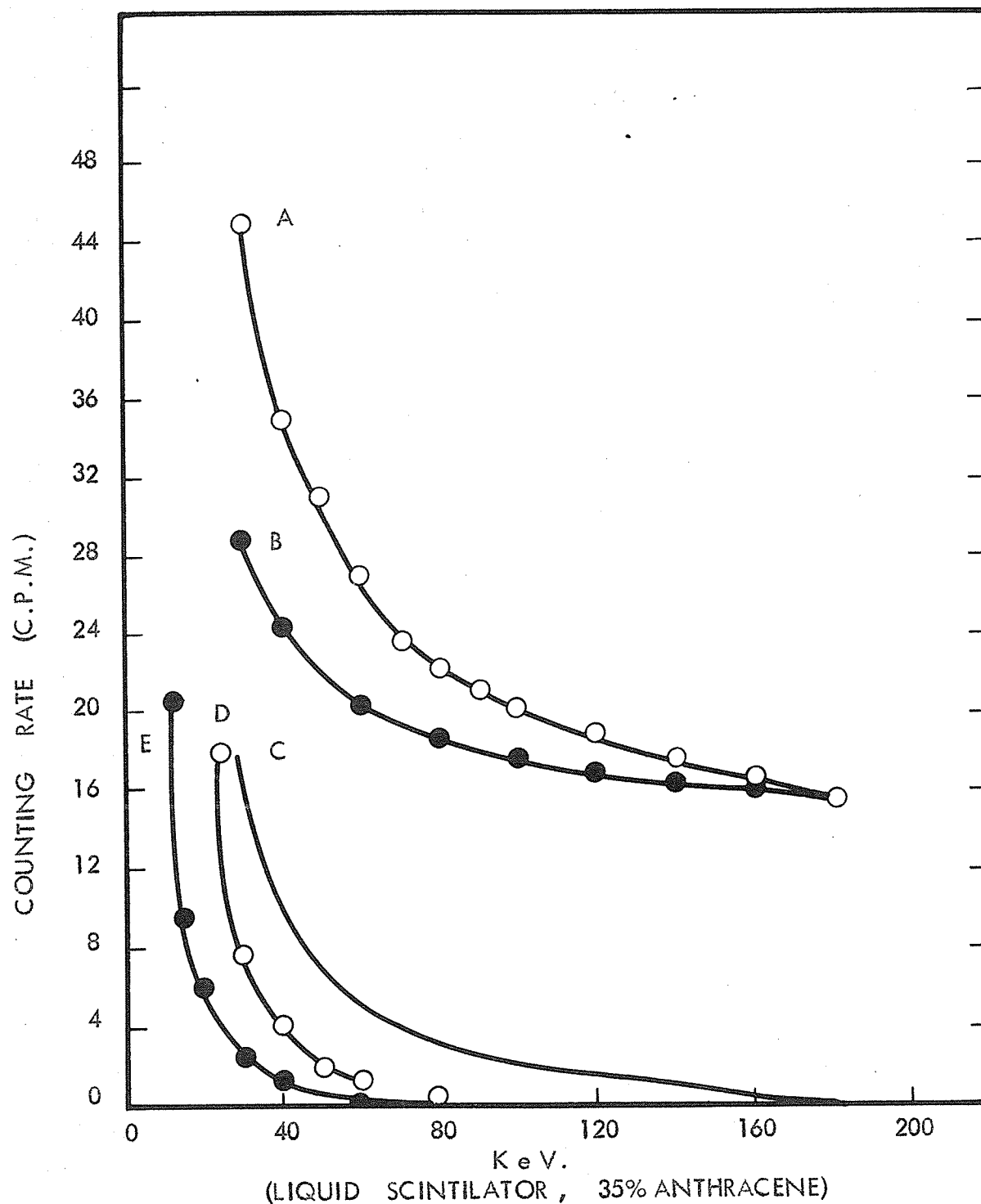


FIG. 7 INTEGRAL BIAS CURVES FOR METHANOL

- A - Modern Carbon Plus Noise D
- B - Old Carbon Plus Noise D
- C - Subtracted Carbon 14 Distribution
- D - Photomultiplier tube (DuMont K1190) Noise Distribution
- E - Photomultiplier tube (DuMont 6467) Noise Distribution

to the same value by means of oxygen bubbling. Thus although the net modern carbon activity is lower the background counting rate is in a much more workable region.

If we again use the criterion of net counting rates in excess of $4 \sigma_B$ being significant the methanol method is meaningful to 30,000 years.

Investigations of the contemporary counting rate for labelled samples of methyl borate were carried out along much the same lines as those on the methanol. In this case the liquid scintillator total weight 24.05 grams, was contained in cell B. Weight of the methyl borate in this scintillator was 7.60 grams corresponding to 2.63 grams of carbon, some of which is C^{14} .

The energy interval chosen for measurement was approximately 45 - 135 kev, which is identical to the interval used in the methanol method. However, since the pulse height efficiency relative to anthracene of the scintillator solution used in the methyl borate method was 45%, a factor which is 10% higher than the scintillator employed in the methanol method, the background counting rate should be lower in the methyl borate method. That this is true is indicated by the values of 10.07 ± 0.08 cpm for net sample counting rate and 4.26 ± 0.04 cpm for background obtained with the above scintillator. Thus, if one invokes the $4 \sigma_B$ criterion the range of the methyl borate method can be estimated as 35,000 years.

In Figure 9 is plotted on a semi-log scale the radiocarbon activity as a function of sample age for each of the three methods of liquid scintillation counting of C^{14} thus far investigated. Curve A is reproduced from the values reported in the literature for the toluene method

of age determination.⁽²⁵⁾ The line slope is determined by the assumed half-life of 5568 years for C^{14} . In all three methods the limits are determined on the $4 \sigma_B$ basis. From this figure it is seen that of the three, the toluene method with a limit of approximately 40,000 years has the longest range; the methyl borate with a limit of 35,000 years is intermediate while the limit of the methanol is the lowest.

(b) Ages of samples investigated

At present a total of six well-documented samples have been dated by means of the methanol and methyl borate methods of radiocarbon dating. Measurements were carried out by Mr. William Turchinetz of the Physics Department at the University of Manitoba and are listed in Table IV, a, b.

Of the six, one sample (S-4 wood), Table IV, a, was dated by the methanol method at a time when the overall signal to noise ratio was favorable; the other five samples were dated by the methyl borate technique.

Measurements of the samples were carried out in the same manner as those to determine the activity of the contemporary samples. Unknown sample and the background sample were alternated every 24 hours bracketting effectively each sample count with two background counts. Total sample counting times of 48 hours were used in all of the methyl borate measurements. The final sample counting rate is given by the mean of the two net sample counting rates.

By using the equation

$$T = 8035 \ln \frac{(R_0)}{(R)}$$

the age of each sample was calculated and the values so obtained are listed

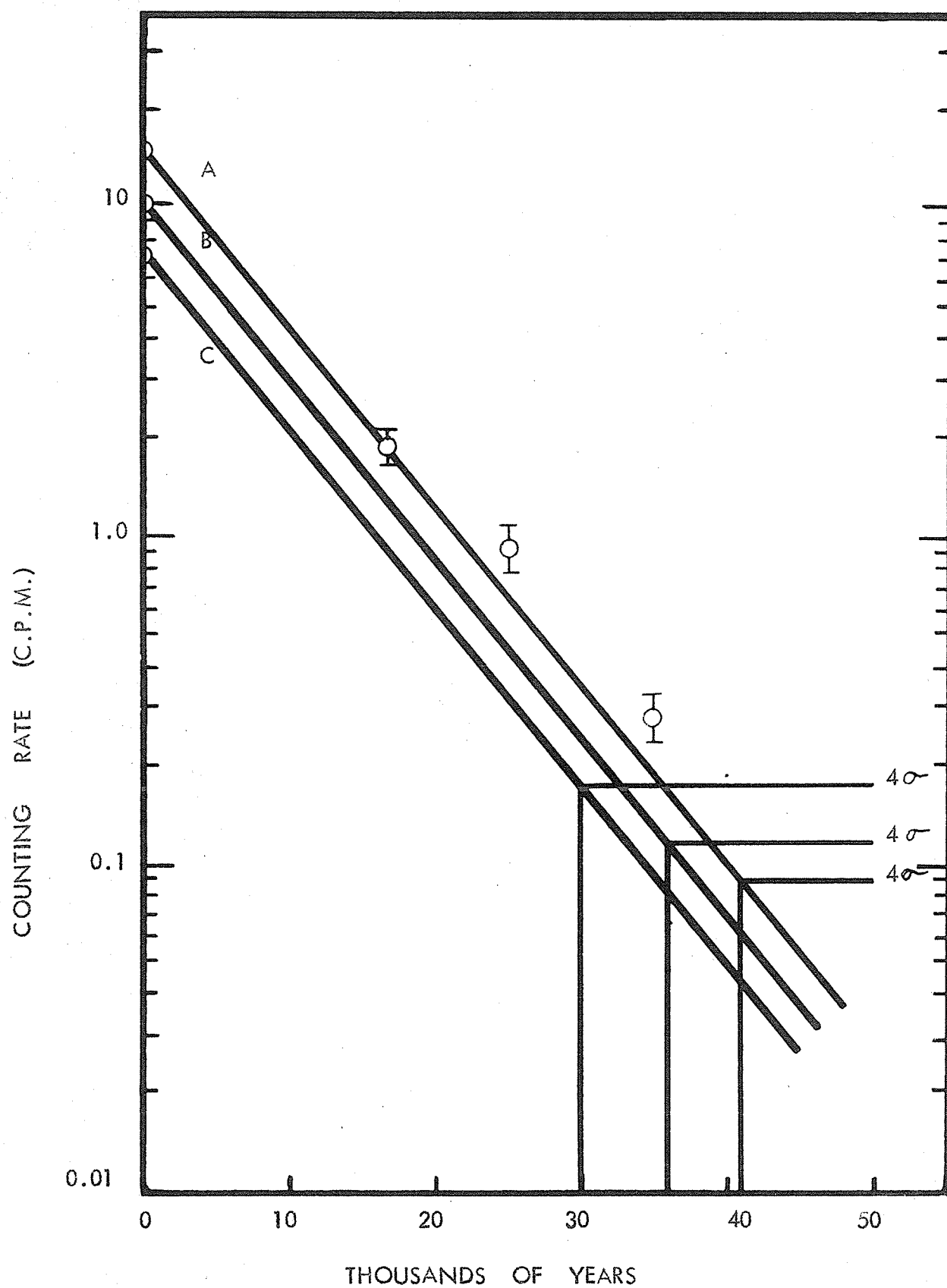


FIG. 9 PERFORMANCE CURVES

A - Toluene

B - Methyl Borate

C - Methanol

in column 7.

Errors in the background and sample counts are given in each case as the standard deviation i.e. $\sigma = \sqrt{n}$ where n is the total number of counts. The errors given for the net counting rate are given as the standard deviation of the net rate and can be calculated by use of the following equation. (23)

$$\sigma_n = \sqrt{\sigma_B^2 + \sigma_S^2} \text{ where}$$

σ_n = standard deviation of net rate

σ_B = standard deviation of background

σ_S = standard deviation of sample

TABLE IV (a)

Age of Sample Using Methanol Method

Sample	Weight of Methanol (grams)	Weight of Carbon (grams)	Net Counting Rate (c.p.m.)	R c.p.m. per gram	Ro c.p.m. per gram	Age (years)
S-4	5.82	2.18	7.15 ± 0.05	3.28 ± 0.04	4.85 ± 0.05	3150 ± 130

TABLE IV (b)

Ages of Samples Using Methyl Borate Method

Sample	Weight of Methanol (grams)	Weight of Carbon (grams)	Net Counting Rate (c.p.m.)	R c.p.m. per gram	Ro c.p.m. per gram	Age (years)
S-3	7.31	2.53	5.34 ± 0.08	2.11 ± 0.03	4.08 ± 0.05	5300 ± 150
S-6	7.40	2.56	$.285 \pm 0.07$	0.11 ± 0.02	4.08 ± 0.05	$29,000 \pm 1500$
S-7	7.65	2.65	$.09 \pm 0.03$	0.034 ± 0.015	4.08 ± 0.05	$38,500 \pm 3500$
S-5	7.52	2.60	$.55 \pm 0.04$	0.21 ± 0.02	$2.85 \pm 0.05^*$	$20,200 \pm 800$
S-8	5.49	1.91	$.505 \pm 0.05$	0.26 ± 0.03	$3.84 \pm 0.05^*$	$21,600 \pm 900$

* Lower values are due to gate width 55 - 60 Kev at Lower level necessitated by electronic instability

DISCUSSION

The suitability of the methanol and methyl borate methods for routine radiocarbon measurements is quite evident. Problems of time and labour involved in preparation of a sample for analysis which, according to Suess,⁽⁴⁴⁾ were the major drawbacks of the liquid scintillation technique, have been successfully overcome in both the methanol and methyl borate methods; the toluene technique, however, involves a somewhat elaborate chemical processing.

Choice of which method is most suitable is governed by a variety of factors. For reasonably quick measurements on carbonaceous samples of small quantity; the methanol and methyl borate methods are obviously the choice. Chief objection to the adoption of the toluene method for routine assay is the number of steps in the chemical synthesis. On the other hand this method is favoured where greater accuracy or age of a very old sample is required.

The possibility of errors due to contamination with carbon from atmospheric CO_2 and isotopic fractionation in the chemical synthesis must be considered. The former problem can be eliminated to a large degree by careful techniques.

A comparison of the background counting rate with the counting rate of a sample containing synthesized "old" methanol showed that the two were identical, within statistical error, indicating that the procedures employed in the methanol synthesis are quite suitable for radiocarbon dating work.

The problem of isotopic fractionation can not be so easily

resolved. Fractionation of the isotopes of carbon is brought about because of differences in their reaction rates.⁽⁴⁰⁾ Baertschi⁽⁶⁾ observed a fractionation factor of 1.011 for $C^{12}O_2$ relative to $C^{13}O_2$ on absorption of a pure CO_2 stream in aqueous barium hydroxide. No measurements have been reported as yet for the C^{14} isotope in this reaction nor for the methanol synthesis. It may be remarked that isotopic fractionation of carbon isotopes has been observed in nature. Wickman⁽⁵⁰⁾ reported large differences in carbon isotope content between plants grown in different environmental conditions. Obviously, this factor, along with mixing of the biosphere with the rest of the natural radiocarbon reservoir, will become important in any attempt to extend the precision of dating methods.

A summary of carbon isotope effects has been given by Ropp.⁽⁴⁰⁾ Several important points may be mentioned. In no case can the molecule bearing the heavy isotope react faster. The effects of fractionation are diminished when the relative yield in a reaction is high and the number of steps kept to a minimum; two conditions which the methanol synthesis fulfills. Mass spectrometric measurements carried out by Craig⁽¹³⁾ and quoted by Suess⁽⁴⁴⁾ have indicated that a depletion of the C^{14} isotope occurs during the synthetic steps in the acetylene method. According to Suess, this would introduce the possibility of an error in the age of a sample of ± 80 years. Such an error is insignificant for old samples but may be important for precision measurements on young materials.

For very old materials, contamination by contemporary carbonaceous impurities will present a big problem. This difficulty could be minimized by careful treatment of samples before synthesis and by several cross check dates on the sample.

Some comment may be given on the values of ages obtained for the samples investigated. The measured age of the wood sample S-4 collected in the Micmac terrace, although not near the estimate by Prof. Lougee, was in good agreement with the views of Prof. Love, Botany Department, University of Manitoba, who estimated from a study of the flora of this region an age not in excess of 5000 years.

The age of 20,200 \pm 800 years obtained for S-5, St. Pierre wood methyl borate No. 1, is in remarkably close agreement with a previous date of 20,300 years obtained by the solid carbon method, but is in apparent disagreement with the acetylene date of 40,000 years reported by the Washington group. The explanation of this anomaly may lie in the manner in which the samples were collected, Page 37.

Ages of the other samples have been measured for the first time and consequently no comparison of results with other dating laboratories was possible.

Further tests on well documented samples which have been dated by other laboratories should be used to fully assess the accuracy of the two methods developed.

Although the predictions by Kulp⁽³³⁾ that liquid scintillation counting will make dating feasible back to 100,000 years are highly optimistic, it does seem feasible that, by judicious choice of glass cells with low radioactive content, increasing availability of low noise photomultiplier tubes, and the use of larger volumes of liquid scintillators, the range of accurate measurement may be extended beyond 50,000 years. It must be emphasized that the two primary assumptions in the radiocarbon dating

method; (1) constancy of the cosmic ray flux for the past 50,000 years; (2) mixing of the carbon exchange reservoir is rapid compared to the time scale of the method, must be fully investigated if extension of dating ranges to 50,000 years may be feasible.

Preliminary attacks on this problem have been reported by Kulp^(34 a,b) who compared radiocarbon ages with ionium and historical ages. Although the results suggest constancy of the cosmic ray flux they are by no means conclusive and further tests are essential.

CONCLUSIONS

Chemical techniques suitable for application in routine analysis of radiocarbon content in carbonaceous materials by the liquid scintillation method have been developed and successfully applied.

Two new methods involving the synthesis of methanol and methyl borate from sample carbon have been outlined. The methanol diluent method is capable of giving results which are meaningful to 30,000 years on a $4 \sigma_B$ basis with the photomultiplier tube used. The methyl borate method is capable of giving higher accuracy to 35,000 years under the same conditions.

Steps involved in the synthesis of methanol and methyl borate from sample material have been carefully investigated. Procedures and equipment suitable for the synthesis of methanol on a macro scale and methyl borate on a semi-micro scale were developed. The yields of methanol were substantially increased by employing dilute hydride-diethyl carbitol solutions. The time and labour involved in the syntheses have been reduced to the same level as that of the gas counting techniques.

The effects of the methanol and methyl borate upon the fluorescence efficiency of liquid scintillators were investigated and the variation of fluorescence efficiency with concentration of diluent determined for each.

Ages for six well-documented carbonaceous samples were measured by the two diluent methods developed.

The eminent suitability of the methyl borate and methanol diluent methods for routine radiocarbon dating measurements has been proven. With further refinements, larger cell volumes and better photomultiplier tubes, extension of the measurement range beyond 50,000 years is a distinct possibility.

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