

CHEMICAL TECHNIQUES IN THE LIQUID
SCINTILLATION METHOD OF RADIOCARBON DATING

by

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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

$$R = R_0 e^{-\lambda T}$$

$$\text{or } T = \frac{1}{\lambda} \ln \frac{(R_0)}{(R)}$$

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

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.

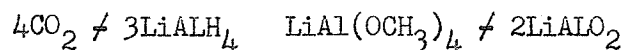
A second method involving the catalytic reduction of CO_2 to methanol at high temperatures and pressures has been described by Tolbert.⁽⁴⁵⁾ Yields of 81-86% on .025 mole scale were obtained, water being the major impurity. No dilution of the labelled material was possible in this method and except for 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 CO₂. Cox et al⁽¹²⁾ demonstrated that even with 100% excess of hydride appreciable amounts of CO₂ 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 CO₂ prepared by the combustion of the sample. The CO₂ is usually generated from BaCO₃ by acids or roasting.⁽¹⁰⁾

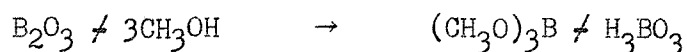
(b) Methyl borate synthesis

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.

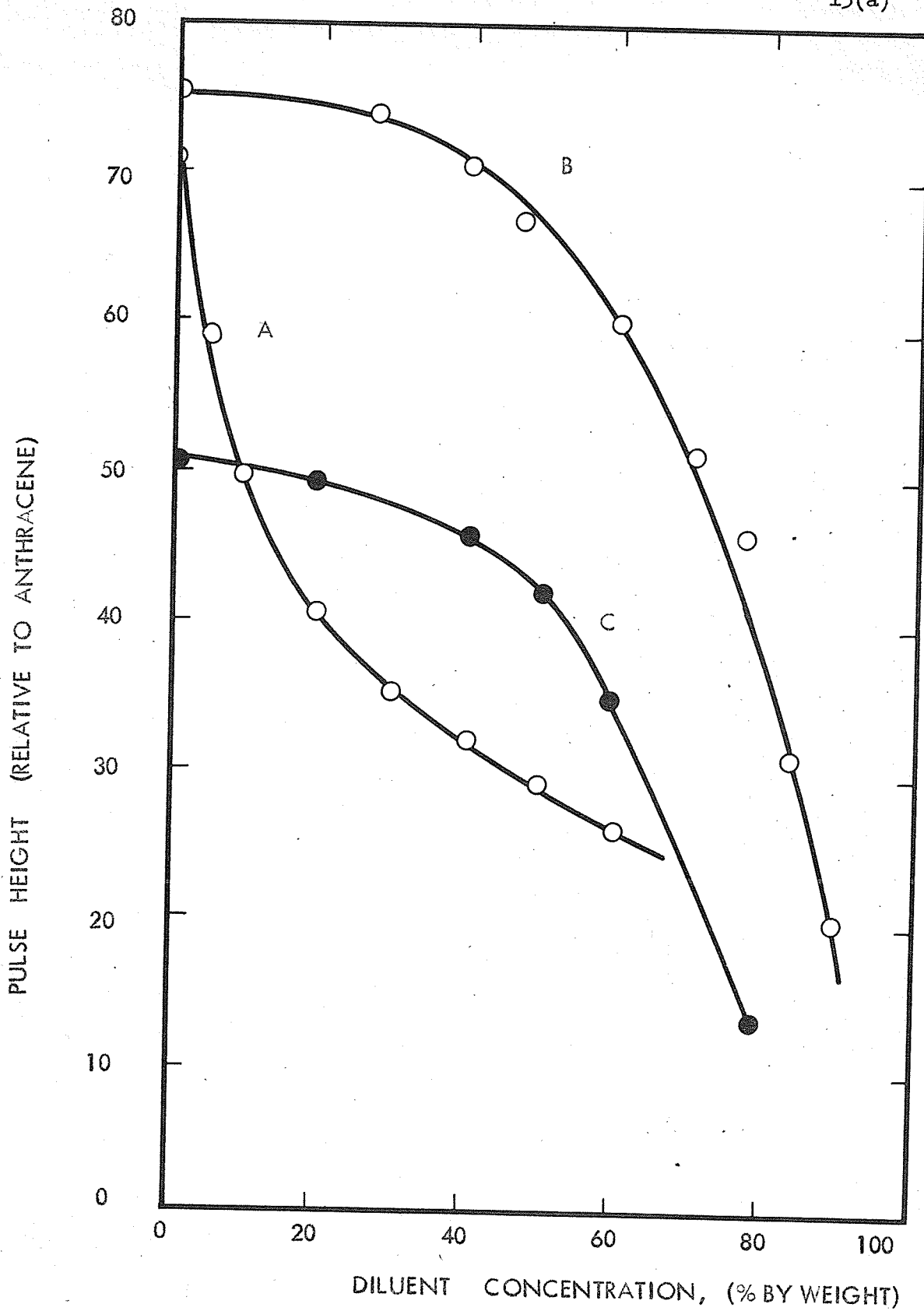


FIG. 1 EFFECT OF DILUENT CONCENTRATION ON PULSE HEIGHT

- 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.