A REVIEW OF RADIOCARBON DATING

AND A STUDY OF TWO LIQUID SCINTILLATION

METHODS

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ABSTRACT

The use of cosmic ray produced radiocarbon to date organic materials of archaeological interest is described from the origins of the method by Libby at Chicago in the late 1940's to the present day. The theory is outlined and sources of error are discussed. The necessity of calibrating the radiocarbon time scale by some independent method is brought out and some of the geochronologies which have been so used (up to 12,000 years) are described. Possible ways of extending the calibration to the radiocarbon limit at about 60,000 years are outlined. The significance of the method to archaeology and its increasing application to geophysical subjects are discussed.

Methods of measuring radiocarbon specific activities are reviewed with particular attention being paid to the liquid scintillation method. The properties of the various materials used in liquid scintillator fluids and the factors governing their choice in a given application are described. Particular attention is paid to the phenomenon of quenching and the means of correcting for it. The various ways by which the radiocarbon may be introduced to the scintillator are examined from the viewpoint of their suitability for dating.

The second part deals mainly with the design and testing of a liquid scintillation system which it was hoped would possess both high sensitivity and convenience. The radiocarbon was introduced as carbon dioxide and counting was performed using the two channel method, with an anti-coincidence screen and 10 cm aged lead shielding. The test program was

terminated before completion by a fire which destroyed the equipment within the shielding. Results obtained, however, do confirm that the method is simple and convenient and seem to confirm the possibility of dating up to about 50,000 years.

Finally a brief test program designed to investigate the feasibility of a simple heterogeneous liquid scintillation system using elemental carbon in granular form is described. The study indicates that this method would be feasible for authenticity checks and possibly dating of more recent objects only if a good low background counting assembly is used. That is, it may be of use as an adjunct to a more sophisticated system but is probably not economic on its own. A material with better optical properties than elemental carbon and with a high carbon content might well be practical and it is suggested that a search be made for such a material.

CONTENTS

FIGURES

The Radiocarbon Dating Method

1.1 Introduction

One of the most important elements present on the surface of the earth is carbon. It is indispensible to the development of life. The large amount of carbon present is dispersed fairly uniformly throughout the atmosphere in the form of carbon dioxide, the biosphere in the form of organic complexes, and in the oceans as carbonates and bicarbonates.

Natural carbon contains the two stable isotopes ^{12}C and ^{13}C and the radioactive isotope ^{14}C, i.e. radiocarbon. ^{12}C is by far the most abundant. The isotopic ratio $^{13}C/^{12}C$ is of the order 0.011 while $^{14}C/^{12}C$ is only around 10^{-12}. The actual values of the isotopic ratios will vary according to the origin of different samples as isotopic separation may take place in the exchange processes between one part of the environment and the other.

The use of radiocarbon for dating arose naturally following the development of sensitive radiation counting systems during World War II. The potential of the method was realised and its general principles established by Libby and his associates, at the University of Chicago, during the period 1945-1952[1,2]. At this time the only application envisaged was to archaeology where it was hoped that a system of firm dates could be obtained for samples whose ages were known previously in a general way from archaeological evidence.

The success of the method as a means of dating rests on the validity of a number of assumptions.

(a) The radioactive isotope, ^{14}C, is produced continuously in the atmosphere by cosmic ray action.

(b) The rate of production is constant over the period to be dated.

(c) The ^{14}C is rapidly dispersed (as $^{14}CO_2$) and mixed throughout a reservoir consisting of the atmosphere, the biosphere and the oceans.

(d) A sufficiently long time has elapsed to ensure that an equilibrium value of the ratio of $^{14}C/^{12}C$ has been attained.

(e) A state of dynamic equilibrium exists between the carbon in the biosphere and that in the surrounding environment. Thus the $^{14}C/^{12}C$ ratio in the biosphere is constant and bears a fixed relation to the value in the environment. It is not necessary to assume that the two ratios are equal and in fact it has been demonstrated that isotopic fractionisation takes place[3,4,5].

(f) The mutual exchange between biosphere and environment is terminated at death. Thus the $^{14}C/^{12}C$ ratio will decline exponentially from death to the present.

The age of a given organic sample is then determined by comparing the ^{14}C specific activity of the sample with that of the standard representing the $^{14}C/^{12}C$ ratio of living organic material.

i.e. $Age = \dfrac{T}{0.693} \log_e \left(\dfrac{A_{standard}}{A_{sample}}\right)$

Taking the currently accepted value of the half-life of ^{14}C as 5730 ± 40 years[6-10], it is seen that the specific activity of the sample has fallen to 0.1% after 9 half-lives (51,570 years). This represents an exceedingly small amount of radiocarbon and effectively limits the radiocarbon time scale to a maximum value of some 50,000 to 60,000 years.

It is not surprising that in the period immediately following the early work attention was focussed on the dating of a large number of samples of widely differing ages and locations. This activity threw up the need for care in the application of the method and various sources of error became evident. It was obvious that if reliable results were to be obtained, and confidence in the radiocarbon method retained, some independent check on the radiocarbon dates was essential and in the 1960's increasing efforts were made to provide this[11-21,53] This work demonstrated that there were considerable deviations between radiocarbon dates and calendar dates and interest has, to some extent, turned to the investigation of the causes of such deviations[23-36,52]

Although the original purpose for the provision of a radiocarbon date versus calendar date calibration was to restore confidence in the radiocarbon method of archaeological dating this latter work has demonstrated that measurements of radiocarbon have also important applications in geophysics, geology, climatology and oceanography[37].

1.2 Foundations of the Method

Essentially the radiocarbon method depends on the continuous production of the radioactive isotope carbon-14 in the atmosphere. A possible mode for this is the reaction

$$\,^{1}_{0}n + \,^{14}_{7}N \rightarrow \,^{1}_{1}H + \,^{14}_{6}C$$
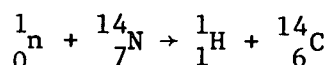
which was first demonstrated in the laboratory by Kurie in 1934[38]. In his experiment Kurie used a beam of deuterons of 3 Mev energy to produce fast neutrons via the reaction $^{9}Be\,(d,n)\,^{10}B$.

It was readily demonstrated that the reaction was exothermic with a comparatively large cross section (1.8 b for thermal neutrons[39]) and it was to be expected that if a flux of neutrons of slow or thermal energies was present then the ^{14}C would be produced in appreciable amounts.

Two competing reactions which are also possible[40,41] are

$$n + {}^{14}_{7}N \rightarrow {}^{4}_{2}He + {}^{11}_{5}B$$

$$n + {}^{14}_{7}N \rightarrow {}^{3}_{1}H + {}^{12}_{6}C$$
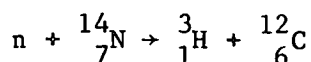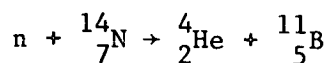
The former does not produce a radioactive product and anyway has a relatively small cross section at all energies of interest. The latter is endoergic (Q = -4.3 Mev) and has a small cross section even for energetic neutrons. It is, however, of some interest as a source of radioactive tritium, $^{3}_{1}H$. Tritium decays with a half-life of 12.46 years to the rare isotope of helium, $^{3}_{2}He$. Although the tritium is too short lived to be of much use for dating it may be used as a tracer to investigate the mixing processes in the atmosphere and oceans and the movement of ground water under the land. The stable end product of the tritium decay, $^{3}_{2}He$, will accumulate in the atmosphere and a measure of its relative abundance should give some measure of the integrated neutron flux to which the atmosphere has been exposed over the millennia and hence provide some evidence for its continuity.

That neutrons were present in the atmosphere as part of the cosmic rays was demonstrated by Korff and Hammermesh 1946[42] who also investigated the variation of neutron flux with altitude. Since the free neutron disintegrates to a proton, an electron and an anti-neutrino with a half-life of 12 mins it is evident that the neutron component of cosmic rays

must be mainly of atmospheric origin with possibly a small solar component present. Confirmation of this was provided by Yuan[43] who showed that the fast neutron flux did in fact fall off near the top of the atmosphere.

The primary cosmic rays are now known to consist of some 85% protons and 15% heavier particles, mainly alphas. The highly energetic primary particles interact, in a variety of modes, with the particles at the top of the atmosphere, to produce, among other things, very fast neutrons. Some 10% of these are captured and transmitted by fast interactions and the rest may be slowed down. Probably around 10% survive the slowing down process[44] and are available for the production of radiocarbon. The primary flux traverses the solar system and will interact with the solar wind flowing out from the sun. The primary flux reaching the neighbourhood of the earth will thus have been modulated by the solar wind and the degree of modulation will depend on the intensity of the solar wind which follows the 11 year sunspot cycle. Near the sunspot maximum the solar wind will be at its most intense and most effective in sweeping out primary particles which would otherwise reach the earth. Near to the earth the charged cosmic ray particles will also come under the influence of the earth's dipole magnetic field.

The rate of production of radiocarbon will thus depend on the interstellar cosmic ray flux, the intensity of the solar wind, and the earth's magnetic field. The earth's field will, in addition to altering the average world wide rate of production of radiocarbon, produce a variation with latitude[45]. Provided efficient atmospheric mixing can be assumed this variation with latitude will not be important for dating.

There seems no good reason to expect fluctuations in the inter-stellar cosmic ray flux over the period of interest (60,000 years) and this has been confirmed by studies of the cosmic ray induced activity of meteorites which have spent most of their lives far from the sun[46]. Fluctuations do however occur in the solar wind and in the earth's dipole field. In addition to these modulation effects the cosmic ray flux will be augmented by protons emitted by the sun especially during a solar flare. This latter effect is likely to be relatively small[44,47].

Given that there will be changes in the production rate of the radiocarbon the crucial question for dating is then whether such changes will significantly alter the $^{14}C/^{12}C$ ratio in the environment. Obviously with a half-life of 5730 years for the decay of ^{14}C considerable inertia will exist in the system and rapid changes in the production rate will not be noticed. The total amount of the dilutant, ^{12}C, in the reservoir is also of vital concern. Since the oceans contain by far the greatest part of the carbon inventory (87%[1]) it is essential to confirm that they do form part of the reservoir and to investigate the rates of carbon exchange between atmosphere, surface layers of the ocean, and the ocean depths.

Mixing within the atmosphere itself is rapid and is readily demonstrated by measurements of the $^{14}C/^{12}C$ ratio at various latitudes[2,48,49]. Such measurements show that the variation with geographical location is small and usually less than 1% despite the strong dependence on latitude of the rate of radiocarbon production due to the earth's field. Exchange rates between the atmosphere and the ocean surface layers have been examined by observing the changes

in ^{14}C concentration produced by the combustion of fossil fuel (Revelle and Suess[25,28]) and by nuclear tests (Bien and Suess[29,30,57].) These tests show that mixing with the surface layers of the ocean is fairly rapid with a maximum period of 20 to 30 years. Mixing with the ocean depths, on the other hand, is relatively slow (Bien, Rakestraw and Suess[31]) and seems to take place by definite ocean currents rather than by exchange through the thermocline. The age of deep ocean water thus depends on the ocean and varies from around 800 years for the Atlantic[55] to 2000 years for the Indian and Pacific Oceans[31].

This longish time for complete mixing in the reservoir does mean that a sudden change in radiocarbon production rate will produce initially a greater change in ^{14}C/^{12}C ratio in the atmosphere than would be expected. Thus the increase in radiocarbon due to the testing of nuclear weapons in the atmosphere in the 1950's led to almost a 100% increase in the ^{14}C/^{12}C ratio in the atmosphere[18]. As mixing proceeds this will fall rapidly to some 3% which will then decay exponentially with the ^{14}C half-life of 5730 years.

From these arguments it would appear that the ^{14}C/^{12}C ratio will have been subject to long term variations over the centuries due to changes in the earth's magnetic field plus shorter term effects due to periodic changes in the solar wind. In addition climatic changes over a long time scale will undoubtedly alter the mixing processes in the reservoir and possibly the total amount of carbon in the reservoir. Such changes in climate can themselves be correlated with solar activity. Dates obtained by the radiocarbon method and assuming constant ^{14}C/^{12}C ratio will therefore be in error by varying amounts and it is essential both from the archaeological, and from the

geophysical viewpoint, to establish the magnitude and nature of these errors by some independent system of chronology. Various methods of doing this are discussed in section 1.3.

Two other sources of error of recent origin are the Suess effect and the Bomb effect. The former[24,145] is due to the large scale burning of fossil fuels over the past 100 years which has released large amounts of ^{12}C to the atmosphere with a consequent reduction in the $^{14}C/^{12}C$ ratio. Currently the ratio is depressed by some 3% (Houtermans, Suess and Munk[28]). The bomb effect refers to the substantial increase in atmospheric ^{14}C arising from the nuclear weapons tests. Small local variations will also exist in the vicinity of nuclear power stations due to $^{14}CO_2$ in the effluent[58]. Both the bomb and Suess effects are avoided by using as a standard a sample which has been calibrated against wood of known age and previous to the large scale burning of fossil fuels. An oxalic acid standard is available which has been normalised using 19th cent. wood.

Essential to the calculation of ages by the radiocarbon method is a knowledge of the half-life of ^{14}C. Unfortunately the value adopted by most of the earlier experimenters of 5568 ± 30 years (Libby[13]) was later found to be somewhat low. Subsequent experiments[6,7,8] produced a value of 5730 ± 40 years which if accepted implies that the early dates are all too young by some 3%. To avoid confusion the Fifth International Conference on Radiocarbon Dating, 1962 recommended that all dates should continue to be calculated in terms of the Libby half-life of 5568 years and expressed in year B.P. (before present).

The present being defined as 1950 AD[9]. This recommendation was
reconfirmed by the Sixth International Conference on Radiocarbon
and Tritium Dating, 1965. A more recent determination of ^{14}C half-
life was reported by Bella, Allisso and Frattelli[10] as 5660 $\pm$ 30
years which would seem to confirm that the Libby value was too low.

1.3 Geochronologies

The theory for the production and decay of radiocarbon described
in the last section suggests various mechanisms which would lead to
a variation of the $^{14}C/^{12}C$ ratio with time. In all cases, however,
it is difficult to obtain evidence of what has happened in past ages
and hence to calculate the value of the carbon ratio. Evidence for
the variation of the carbon ratio must therefore come in the first
instant by comparing radiocarbon dates with astronomical dates and
to do this chronologies which do not depend on radiocarbon must be
developed.

The ideal system would be that in which all the dates were fixed
by historical evidence although even this may be, on occasion, in
error. The bulk of such evidence is, of course, restricted to the last
2000 years. The first comparison of historical and radiocarbon dates
was that of de Vries in 1958[11] which showed a maximum discrepancy around
the year 1690 AD. The error was very large with the radiocarbon
method giving dates as much as 150 years too young. De Vries
speculated that this maximum was related to the advance of the glacier
system which had reached a maximum some years previously around 1670 AD.
Extension of this chronology back to the time of Christ shows a number
of apparent oscillations with a period of some 150 to 200 years.

Historical evidence beyond this period comes mainly from ancient

Egypt and therefore rests heavily on the assumption that the world-

wide distribution has always been substantially uniform. Suess[19] has

extended the historical chronology to 3300 BC approximately by using

a series of Egyptian samples and it seems likely that this represents

the limit attainable by this procedure.

A check on the accuracy of the historical dates is provided by

dendrochronology or dating by counting tree rings. It is assumed that

the carbon in a given tree ring is locked in the wood after the year

of formation. The age of the ring is obtained by counting rings and

comparing related specimens. The techniques for doing this are now

well developed and the calculated dates are accurate to within a few

years.

Various dendrochronologies have been established using different

types of wood from different localities. Trees which have proved

suitable are the ponderosa pine from Arizona, the California giant

redwood or sequoia[14,53] and the New Zealand kauri[17]. This work has

provided adequate confirmation of the deviations in radiocarbon dates

already noted from historical chronologies. The oldest date attainable

with the trees mentioned is around 1300 BC with the sequoia. However,

the refinement of dendrochronological techniques has made it possible

to use an even older tree, the bristlecone pine or pinus aristata of

California. The bristlecone pine is of entirely different form to the

giant redwood. It is low and consists of a mass of twisted stems often

covering a considerable area. The dating of a particular sample

requires a great deal of painstaking work. However, with its help a

dendrochronology dating back to 4100 BC has been established[16] and

it seems likely that this will be extended by at least a further

millenium.

Various chronologies exist from 5000 BC to around 10,000 BC

(the last ice age) but they are not always in agreement. The oldest

method is probably the varve chronology first outlined by de Geer[59]

in 1910. A varve is a deposit of clay and sand left in a lake by

the annual meltwaters from a glacier and the method consists of

identifying and counting the annual varves. A fairly comprehensive

chronology has been established in the Scandinavian region   and

various partial chronologies exist elsewhere.

A chronology based on the rate of sedimentation in lakes was

described by Stuiver in 1967[18]. This was based on three separate

lakes in Asia, Africa and America, and extends to 8000 year BC.

The agreement with the dendrochronological data up to 4000 years BC

is good but a considerable discrepancy exists with the varve chronology

at dates older than this.

A limited amount of data is also available from various other

sources such as thermoluminescence of ancient pottery[60], remnant

magnetism of bricks[34], pollen deposits in peat, guano deposits in

caves[54], radiocarbon dating of ice layers on the permanent ice caps[61]

and so on.

Beyond the last ice age, i.e. previous to about 12,000 years BC

up to the limit for radiocarbon dating at about 60,000 years, no really

reliable data exists. Various consistency checks can be applied to

data from different parts of the world, partial chronologies can be built up from early varve deposits, but it is not as yet possible to establish a comprehensive chronology. Dating systems based on radio-isotopes other than ^{14}C have been suggested. The isotopes ^{10}Be with a half-life of 2.5 million years and ^{26}Al with a half-life of 0.75 million years have been studied[62,63]. However, both of these are cosmic ray produced isotopes and accordingly are subject to the same uncertainties as radiocarbon. The existence of uranium in sea water and the different precipitation rates of the various stages in the uranium decay chain provide a possible method of dating by the measurement of isotope ratios in the ocean bed sediments. Two ratios which show promise are the ionium-thorium ratio $(^{230}Th/^{232}Th)$[64] and protoactinium-ionium ratio $(^{231}Pa/^{230}Th)$[65].

Data from the papers by Stuiver and Suess[15] and by Stuiver[18] are presented in figures 1 and 2 for the first 10,000 years BC. It will be noted that although only one radiocarbon year exists for a given calendar year the reverse is not true especially in the last 500 years. Both a short term and a long term variation is evident. It is suggested that the short term fluctuation is most likely related to solar activity while the long term one is due to a slow variation of the earth's dipole magnetic field.

FIGURE 1

RADIOCARBON AGE — TRUE AGE VARIATION
FOR THE LAST 1000 YEARS
(STUIVER AND SUESS [15])
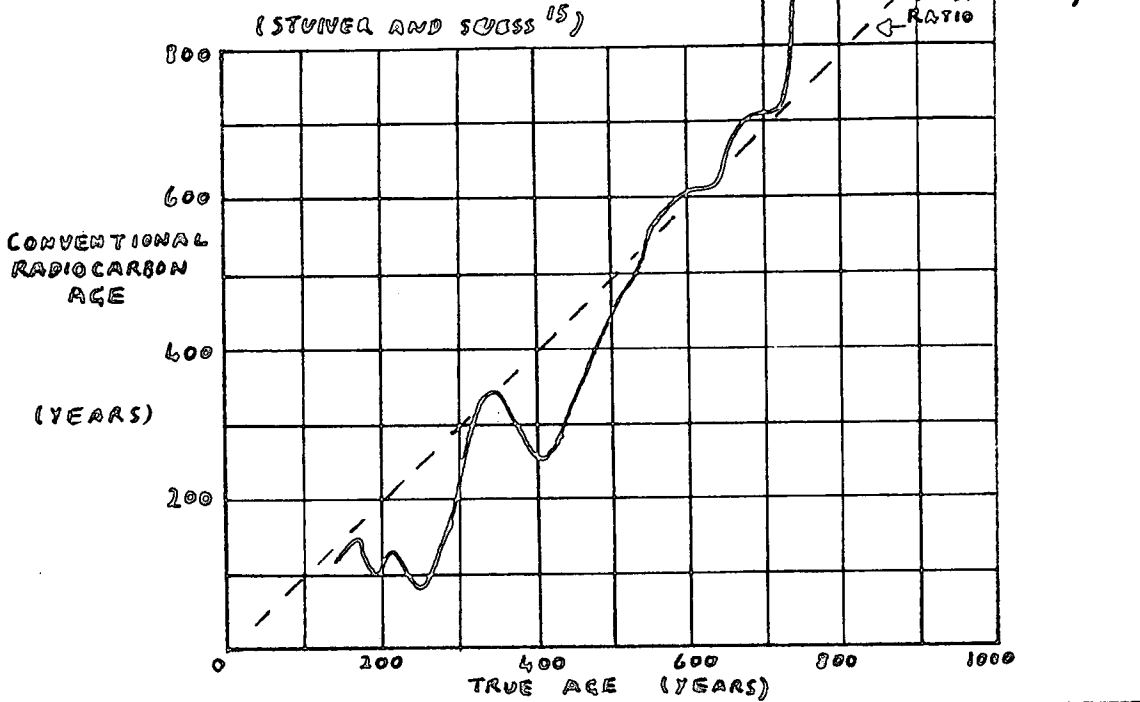
FIGURE 2

RADIOCARBON AGE — TRUE AGE VARIATION
FOR THE LAST 10000 YEARS
(BASED ON DATA FROM STUIVER [18])
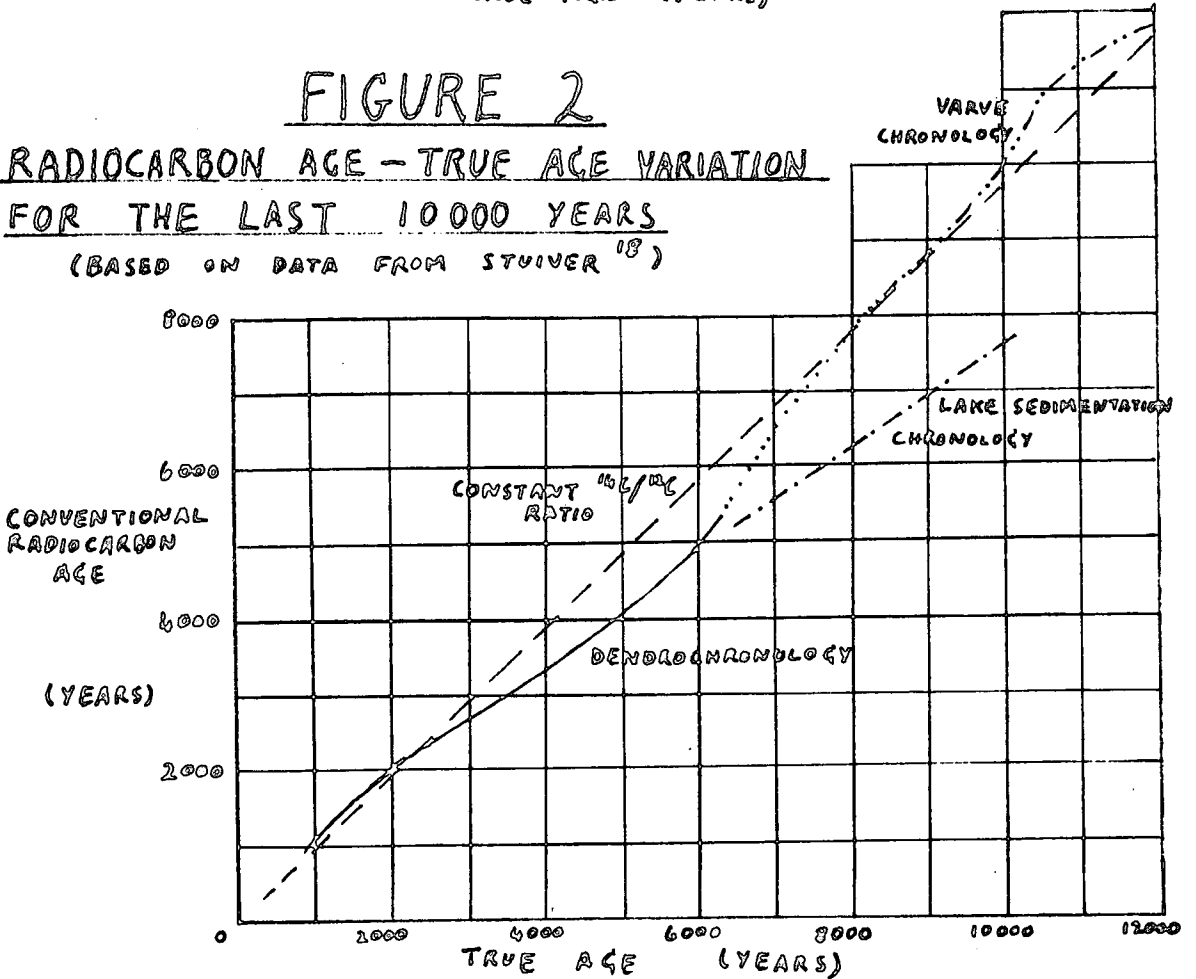
1.4 The Significance of Radiocarbon Dating to Archaeology

Archaeology is concerned with the discovery, recovery and study of human remains and artifacts especially from prehistoric times. From such work attempts are made to construct a picture of the way of life of the people concerned, to trace the development of their culture and to link this with other groups in widely differing geographical locations and in different epochs. The source material is of necessity limited and it is essential that the maximum amount of information be extracted from it.

A series of samples from the same site can usually be placed in correct historical sequence fairly easily. However, where gaps exist in the sequence or where samples come from widely separated sites then great difficulty may be found in arriving at the correct order. Yet it is essential that such an order of time be established if the relationship between different cultures is to be fully understood. In view of the fact that samples may come from different continents the only sure way of resolving the problem is to have some means of fixing the age of any sample on an absolute time scale preferably based on the movement of the earth round the sun.

Various methods exist for the establishment of sample dates. Geological evidence based on sedimentation rates, glacier movements and so on may be used to date the site in which the sample was found. Geological dating of this type involves a long time scale and will not normally be sufficiently precise for our purpose even although development rates of the early cultures are themselves very slow. Careful excavation with attention to stratification enables samples from the

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same site to be ordered and studies of the cultural and artistic merit of objects found will often allow comparison with other sites. Despite the apparent uncertainties inherent in such methods it is possible to achieve a certain amount of success with them, but the need for some independent and precise system of dating remains obvious.

The radiocarbon method when it appeared seemed to fulfil this need. Many archaeological anomalies were removed and problems solved by the dating experiments carried out in the early years. At the same time a number of apparent new anomalies appeared and this led to a certain amount of criticism of the method. This period of disenchantment was probably due mainly to a failure of communication between the two disciplines involved. On the one hand the archaeologists tended to accept the radiocarbon dates uncritically as absolute figures without fully appreciating the errors which were implicit in the method. On the other hand the scientists in the radiation laboratories did not always appreciate the importance of the past history of the sample, the nature of the site, the possibility of contamination and so on.

The true significance of the radiocarbon method to archaeology must be that it is a very useful source of information which may be used to fix dates.[54] However, it must not be taken in isolation but only along with all other available facts, whether geological, archaeological or physical. The uncertainties of each part of the evidence must be assessed and a date arrived at which depends on the whole of the evidence.

1.5 Future Trends

The realisation that radiocarbon dates did not in general correspond with calendar dates and that the $^{14}C/^{12}C$ ratio was not in fact constant led to an intense study of the mechanisms by means of which radiocarbon is produced and dispersed throughout the reservoir. This in turn has greatly increased knowledge of cosmic ray phenomenon, atmospheric mixing, interchange between atmosphere and ocean, oceanic mixing and associated problems. In fact, the cosmogenic radiocarbon, and latterly the bomb test radiocarbon, has permitted tracer experiments to be carried out on a grand scale. Models of the mixing and exchange processes have been described and no doubt more refined versions will appear. It seems likely that in the future this trend will continue and such radiocarbon tracer experiments will further improve our knowledge of movements of the atmosphere and of the oceans.

Continued efforts will also be made to extend and improve the calibration of the radiocarbon time scale. This will not only be of value to archaeology but by detailing the changes in $^{14}C/^{12}C$ ratio which have taken place will provide information about changes in both the prehistoric climate and magnetic field of the earth.

Purely in the archaeological field improvements should be possible in the techniques of retrieval from the field so as to reduce contamination and also in the extraction of carbon from difficult materials such as bone. Until such improvements are achieved the requirement from the radiocarbon counting laboratories will be for increased convenience and reliability rather than sensitivity.

The development of counting equipment of higher sensitivity will however make it possible to assay other radioisotopes present in very low abundance. This will enable new dating systems based on these radioisotopes to become established and help fill the gap between the limit of the radiocarbon method at some 60,000 years and the youngest dates possible with the potassium-argon dating method of around one million years.

CHAPTER 2

Measurement of Radiocarbon Specific Activities

2.1 Survey of the various methods

The specific activity of radiocarbon in modern organic material

(corrected for Suess and bomb effects) is approximately 15 min^{-1} g^{-1}[58].

After 5 half-lives (28,650 years) this has fallen to 0.5 min^{-1} g^{-1} and

after 10 half-lives (57,300 years) to 0.01 min^{-1} g^{-1} and the measurement

of such low specific activities poses a difficult problem.

When the radiocarbon technique was first considered by Libby and

his associates no counting system existed which could hope to detect

and measure the radiocarbon. In this situation three general approaches

to the problem are feasible. These are (1) reduction of the ratio of

the background to sample counting rates, (2) improvement in counting

efficiency, and (3) increase in sample specific activity by isotope

enrichment prior to counting.

In the initial experiments the third of the approaches was used.

Methane gas was obtained from the sewage system of Baltimore. This gas

was evolved from material which had only recently left the biosphere

and so contained radiocarbon at the environmental concentration. For

comparison a separate sample of methane from a petroleum source which

would contain virtually no radiocarbon was used. The methane was

isotopically enriched in a thermal diffusion column by A.V. Grosse and

then counted in an ordinary cylindrical Geiger tube by Libby's group[66,50].

The enrichment achieved was determined by measuring the $^{13}C/^{12}C$

enrichment ratio using a mass spectrometer and then calculating the

corresponding $^{14}C/^{12}C$ ratio. Enrichments of over 250 times were

achieved and the experiment successfully demonstrated the presence

of ^{14}C in the methane sample.

This thermal diffusion column isotopic enrichment method, although

successful, was too involved to provide an economic and convenient

system for routine measurements. In order to avoid the preliminary

isotope enrichment, attempts were then made to reduce the background

count rate by using a screen wall Geiger tube in which the sample was

deposited as a thin layer of elemental carbon on the inside of the tube

wall. The use of the screen, maintained at some 90 V positive with

respect to the wall, served to define the sensitive volume which was

limited to about one third of the total length. The section of the

wall coated with the sample was constructed as a cylinder, fitting

loosely within a second outer wall. It was then possible to slide

the sample towards or away from the sensitive volume simply by tilting

the counter. By this means background and sample counts could be taken

with one voltage setting and with one filling of gas.

The background count rate obtained with the screen wall counter on

the open bench was some 500 min^{-1} which completely obscured any count

due to the sample. An eight inch iron shield was then used which

reduced the background to 100 min^{-1} which was still too high. Additional

shielding produced little improvement and showed that the residual back-

ground was either extremely penetrating or due to contamination within

the system. Since it was known that cosmic ray muons would certainly

be the major cause of the external component of background and that

there was little chance of stopping them in conventional shielding

a system of anticoincidence shielding was developed[67].

The anticoincidence shield consisted of a number of long Geiger

counters placed closely together all round the sample counter. Any

muon detected by the sample counter would also have been detected by

one of the shield counters. The outputs from the shield counters were

therefore used to control a gate which effectively shut off the sample

counter for a short time whenever a muon was detected in the shield

(figure 3). The use of the anticoincidence shield reduced the back-

ground count to 5 min^{-1} which was low enough to enable the sample

count to be measured.

It was then realised that the iron used in the shield was itself

contributing to the background by emission of gamma rays which were

not detected by the anticoincidence Geiger tubes due to their low

efficiency for gammas. A further reduction in background was achieved

by Kulp and Tryon[68,69] by the use of a one inch shield of distilled

mercury placed between the anticoincidence screen and the sample counter.

The background count rate was now 2 min^{-1} and with a maximum counting

time of 1 week, radiocarbon ages of up to 30,000 years could be measured.

The residual background was now mainly due to impurities within the

counter materials and as these had already been chosen for purity no

further dramatic improvement could be expected using this system.

FIGURE 3

BACKGROUND REDUCTION BY ANTI-COINCIDENCE SCREENING
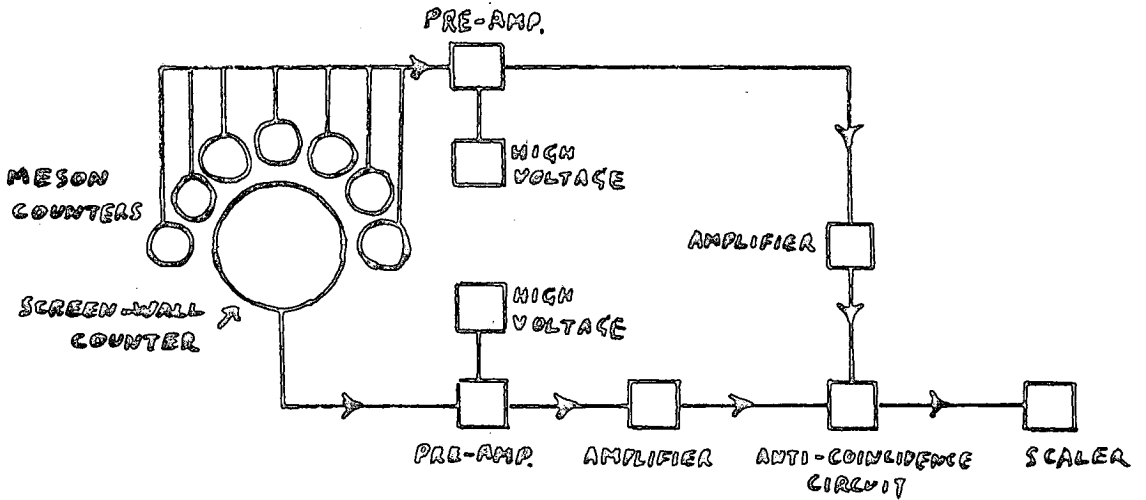
METHOD OF ANDERSON, ARNOLD AND LIBBY [67] 1951

Development of gas handling techniques made it possible to revert
to the earlier practice of introducing the carbon in the gaseous form.
The objection to this previously had been that it was not possible
to exactly reproduce the filling conditions for the two counts, back-
ground and sample. Initially the carbon was synthesised into acetylene
and the counter was operated either as a Geiger tube or as a proportional
counter[70].

The carbon dioxide proportional counter which is the gas counting
system currently in use today was first developed by de Vries and
Barendsen[71]. Carbon dioxide had the great advantage that is it was
easy to produce and to handle. Although this counter made it possible
to achieve dating over most of the desired period the proportional
counter was sensitive to small amounts of contaminants and great
attention had to be paid to gas purity[72]. There was still a need for
an alternative and more convenient method.

This was provided by the liquid scintillation counter[73]. Arnold,
in 1954, successfully overcame the problems of noise originating in the
photomultiplier and its associated circuit by the use of two photo-
multipliers to view the same scintillator[74]. Any event originating in
the scintillator would be detected by both photomultipliers and could
be picked out by the use of a coincidence circuit (figure 4). Although
modern low noise photomultiplier tubes and electronics no longer make
it essential to use two tubes on all occasions the technique is still
of considerable value whenever greater sensitivities are required.

The liquid scintillation method which was developed initially because of its greater convenience can now rival and even surpass the carbon dioxide proportional counter.

The remainder of this chapter will be concerned with describing the liquid scintillation method and its application to radiocarbon.

2.2 The Liquid Scintillation Method

Liquid scintillation counting became possible with the discovery in 1950 that the dilute solutions of some compounds can emit fluorescent light[74,75].

The scintillation mechanism involves a number of steps which must follow within a few nanoseconds of each other if the particular solution is to be used for counting. The radioactive particle is first absorbed in the body of the scintillator and its energy is partly used to excite molecules of the solvent. The energy so taken up by the solvent molecules is then transferred non radiatively from molecule to molecule until it gets to a molecule of the solute which then may de-excite with the emission of a photon. The wavelength of the emitted light is characteristic of the solute.

In a counting set up the fluorescent light must then be collected and transmitted to the photocathode of a photomultiplier where it is converted to photoelectrons. The photoelectrons are accelerated within the photomultiplier and electron multiplication occurs at each of the intermediate dynodes. Finally a voltage pulse is developed at the collector (anode) and passed on to the electronics for amplification in the usual way. The height of the final output pulse should be

proportional to the energy originally absorbed by the scintillator. However, since both the scintillation process itself and the photo-electric effect are subject to statistical variations the final output will show a statistical spread even for a monoenergetic input[76,77].

For highest counting efficiency the photon yield of the scintillator, the transfer efficiency of light from scintillator to photocathode, and the photo-electron yield must all be high. This requires that the spectrum of the emitted light must match the spectral response of the photocathode and that the intervening material, mostly solvent, should be transparent at these wavelengths. Spectral matching can often be improved by the addition at a low concentration of a second solute emitting at a longer wavelength. Although materials used for this purpose are generally of poor solubility and hence unsuitable as primary scintillators their contribution in moving the emission spectrum of the scintillator towards that required by the photomultiplier is very important. The addition of the wavelength shifter must not, of course, reduce the scintillator photon yield.

One of the most attractive applications of liquid scintillation counting is to the assay of soft beta emitters[78]. Because of the softness of the radiations the isotope must be introduced into the scintillator itself. Many of the labelled compounds to be measured are themselves soluble or easily miscible in the scintillator liquids and the preparation of samples for counting is therefore quick and convenient. In contrast the use of a gas flow proportional counter or ionisation chamber often requires tedious operations to convert the components to an appropriate gaseous state.

The addition of quantities of foreign material carrying the source, to the scintillator, will tend to reduce (quench) the light output. Thus the choice of the correct scintillator mix in a given experiment must also take into account the nature of the source material to be added to it[79]. This is particularly true in the case of radiocarbon dating where the very low specific activity of the source material requires that large amounts of it be added to the scintillator.

The solvent[80] must be selected so as to give, a high light output for the scintillator, solubility for both scintillator and sample, transparency, and possible low freezing point. Solvents were studied extensively by Hayes, Rogers and Sanders in 1955[81] who arrived at a list of some dozen liquids which were suitable. This includes xylene, toluene, phenylcyclohexane, ethylbenzene and butylbenzene. The first two of these, xylene and toluene, have become the normal choices and toluene is usually used as the standard for comparison work. Results are sensitive to the presence of impurities and it is essential that high grade materials are used.

A special problem is presented by aqueous samples which are not miscible in any of the solvents mentioned above. One method is to use 1,4-dioxane with which water is miscible. Dioxane unfortunately does not give a high light output and is subject to considerable quenching by the addition of water. Mixtures of dioxane and xylene will improve the light output and addition of naphthalene will compensate for quenching by water.

Primary solutes (scintillators) and secondary solutes (wavelength shifters) were also studied by Hayes and co-workers[82]. More recently Kowalski, Anliker and Schmid[83] examined a range of new materials which were not available to the early workers. The most commonly used primary solute has been and still is 2,5-diphenyloxazole (PPO). Where a secondary solute has been used this has commonly been 1,4-di-(2-(5-phenyloxazolyl))-benzene (POPOP). Some attention has been turned recently to 2-(4'-t-butylphenyl)-5-(4"-biphenylyl)-1,3,4-oxadiazole (butyl PBD) because of its reported insensitivity to quenching by the addition of other materials (Scales 1967[84]).

Liquid scintillation counting systems may use two photomultipliers in coincidence as in Arnolds apparatus or a single straight through system (figures 4, 5). Because of the lower efficiency of liquid scintillators compared with crystals/ and the lower energies involved when soft beta emitters are measured, the pulse heights from the photomultiplier output will be small. Increased amplification in the external circuit is required and the existence of spurious pulses originating in the photomultiplier (dark current) will confuse the result.

Photomultipliers selected for low dark current are used and the dark current can be further reduced by cooling the photocathode.

In dual input systems spurious dark current pulses are rejected by the coincidence circuit as such pulses arise in one photomultiplier only. A certain amount of noise will still occur due to random coincidences between the two channels and it may still be desirable to reduce the dark currents to a minimum by cooling.

FIGURE 4

NOISE REDUCTION BY THE COINCIDENCE

METHOD

SYSTEM OF ARNOLD[73] 1954
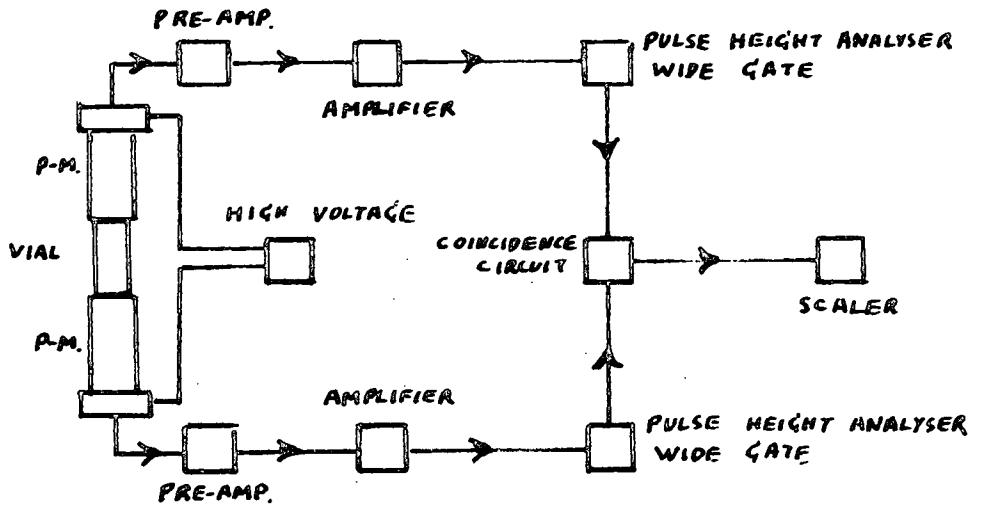
FIGURE 5

SINGLE INPUT COUNTING SYSTEM
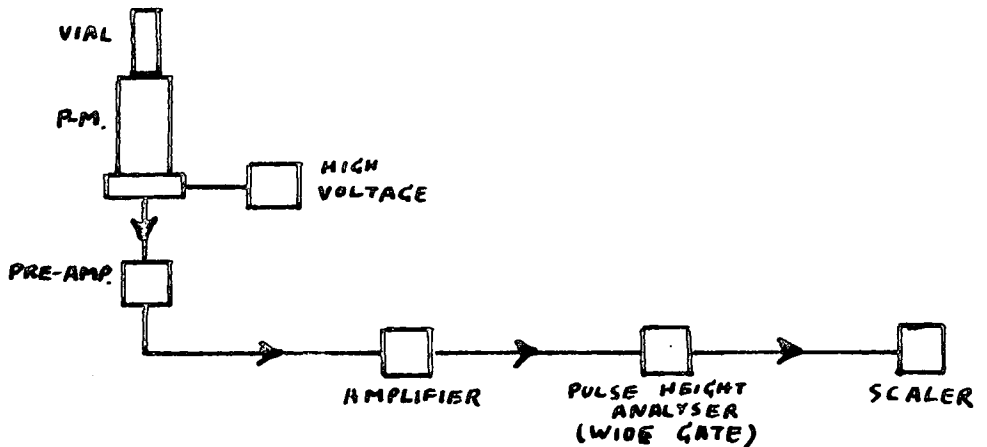
Single input instruments are simple, more convenient and less expensive than dual input instruments. They have also a higher efficiency since all the fluorescent radiation is directed at one photomultiplier. They may therefore be preferred for counting of aqueous samples in dioxane mixtures which have a lower light output. Dual input instruments have a lower background plus noise count rate and hence despite their lower efficiency their sensitivity is greater. Also the dual input system will remove most of the counts due to phosphorescence of the sample bottle and so reduce the waiting time between insertion of the bottle and the start of a count.

Extensive reviews of liquid scintillation counting with bibliographies are given in references[85,86,87].

2.3 Quenching

Quenching, in the context of liquid scintillation counting, describes any process which may reduce the light pulse arriving at the photocathode. Since the conversion of the energy carried originally by the beta particle, to light at the photocathode, involves a number of intervening stages and since any process interfering with any of these stages may reduce the final output it is evident that quenching can arise from a number of different causes. Schwab[88] divides quenching mechanisms into five classes: self-absorption quenching, dilution quenching, chemical quenching, colour quenching, and optical quenching.

Self-absorption, that is the absorption of part of the beta particle energy within the source material, is always a consideration when counting soft beta emitters, and it was the elimination of this factor which was one of the greatest attractions of the liquid scintillation method. However, the absence of self-absorption can be assumed only when the source material is in solution in the scintillator. In the case of suspensions and gels where the source is in particulate form self-absorption will be present and the size of the particles may be an important factor. Self-absorption may also be of importance in the counting of aqueous samples blended with the scintillator in the form of an emulsion.

Dilution quenching is simply due to the addition of a foreign substance to the scintillator which absorbs excitation energy from the excited solvent molecules without a corresponding emission of radiation. Considerable amounts of dilutant are usually necessary to produce significant quenching.

Chemical quenching is the term used to describe any process which interferes with the energy transfer from beta particle to solvent molecule, from solvent molecule to solvent molecule, or from solvent molecule to scintillator molecule. The effects of various chemical quenchers have been examined and are reported by Jaffee and Ford (1970)[89] who also introduced the term Scintillation Attenuation Factor (SAF) defined as the attenuation of scintillation efficiency produced by 1 m-mole of quenching agent. Values of SAF range from 0.004 for methanol to 160 for carbon tetrachloride.

A particular form of chemical quenching pointed out by Pringle and co-workers, 1952[90] is that due to the presence of oxygen. This may reduce pulse heights by as much as 25%. Since oxygen is present in variable amounts in all scintillator solutions prepared or stored in air this effect cannot be ignored. Various methods have been suggested for the removal of the oxygen from solution. The most commonly used is that of Pringle in which the prepared scintillator is bubbled with nitrogen to displace the oxygen prior to sealing and counting. An alternative method used by Mahin[91] was first to freeze the scintillator in liquid nitrogen allowing in the process a few millilitres of liquid nitrogen to enter the vial, then to allow the temperature to rise sealing the vial when gas evolution from the scintillator had ceased. Other methods requiring more specialised equipment are vacuum distillation of the solvent just prior to the preparation of the sample[92] and removal of oxygen by ultrasonic vibration under an inert gas[93].

Colour quenching is the absorption of the fluorescent radiation within the sample vial. Strong colour quenchers appear coloured and the degree of quenching can be assessed by measuring the absorption spectrum of the solution (Ross and Yerick[94]).

Optical quenching arises from variations in the optical coupling between the sample vial and photomultiplier caused by changing the vial. Condensation of water on the vial surfaces in cooled systems may also effect the optical coupling.

2.4 Quench Corrections

The effect of quenching on the count rate recorded in a counting
system is illustrated in figure 6. The reduction in the heights of
pulses shifts the whole spectrum towards the lower energy end. In the
simple system with a discriminator at the low energy end count rates
decrease as quenching increases. In a one counting channel system
count rates first increase and then decrease, while in a two channel
system the ratio of the count rates in the lower to the upper channel
will increase as quenching increases.

Since it is exceedingly difficult to ensure that quenching remains
unchanged from sample to sample especially in a series of routine
measurements it is essential to have some means of assessing the degree
of quenching of each sample[95,96]. Once this is known then either the
system is adjusted to compensate for the quenching or the results are
corrected afterwards by calculation. Adjustment is achieved by varying
the photomultiplier high voltage supply, or the external amplification,
or the analyser gates.

The most direct means of assessing quenching is by the internal
standard method. The standard, whose activity is known, is added to
the sample vial after the initial count and a second count taken. From
this the efficiency of the system can be calculated and a suitable
correction made. The internal standard method is inconvenient in use
and is not suited to routine or automatic systems. Also it results in
the loss of the sample and the standard with each experiment.

FIGURE 6

QUENCHING IN LIQUID SCINTILLATION COUNTERS

BASED ON DIAGRAMS BY VON SCHWAB[88] - ATOMPRAXIS 12 1966

SINGLE CHANNEL METHOD

UNQUENCHED SPECTRUM

EFFECT OF QUENCHING
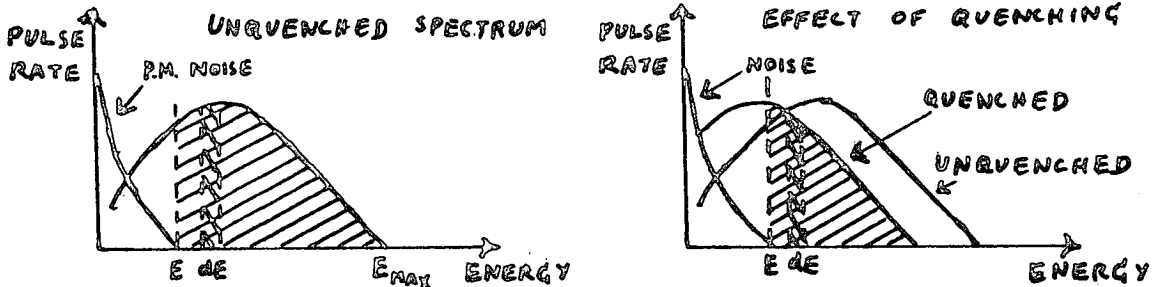
EFFECT OF QUENCHING ON COUNT RATES

CHANNEL RATIO METHOD

TYPICAL QUENCH CORRECTION CURVE
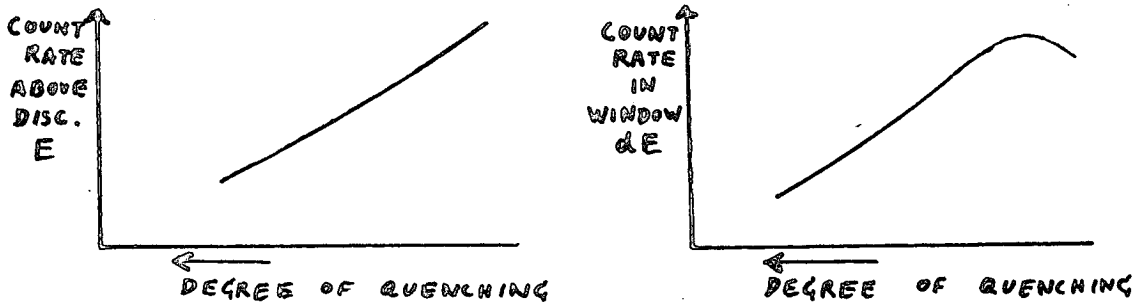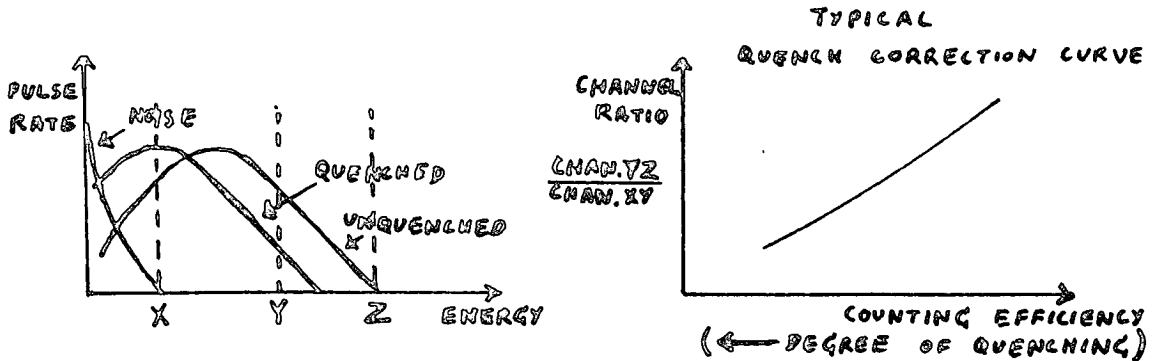
A variation of this method is the internal standard with identical system properties[97]. In this case the source material is divided into two equal parts. Two vials are prepared, one containing source only and the other source plus internal standard. Great care is taken to ensure that the two aliquots are identical in their chemical and quenching properties and that the vials are themselves identical. The two counts can then be taken in succession and effects of instrumental drift are minimised. At least half of the sample material may be preserved for subsequent counting.

Various methods are available which do not involve the use of a standard source.

Balanced quenching[98,99,100] means that the count window is restricted to that part of the spectrum where quenching has least effect. The balance point is found by drawing a series of curves of count rate against discriminator voltage for samples with increasing amounts of quencher added. The centre of the count channel is then chosen so that the positive and negative deviations of the quenched samples are uniformly distributed about the unquenched sample. No further correction for quenching is then necessary. Unfortunately no true balance point exists and so there will always be some residual error. Also because of the limitation of the counting channel the efficiency will always be low.

The extrapolation method is capable of much greater precision and although somewhat tedious is often the preferred method for absolute counting. Samples containing increasing amounts of the source material are prepared and counted. The apparent specific activity, that is the

count rate divided by source concentration, is calculated in each case and plotted semi logarithmically against the concentration. The resultant graph is approximately a straight line and can be readily extrapolated to zero concentration to give the unquenched specific activity.

In the dilution method a series of samples of different concentrations are prepared. Each sample is diluted with increasing amounts of scintillator solvent until a maximum count rate is reached. These maxima are plotted against source concentration and extrapolated to obtain the unquenched count rate. This method is very laborious and is not effective with highly quenched samples.

The channels ratio method can be used for a series of experiments on the same isotope. Two counting channels are chosen to cover the spectrum to be measured. The channel counting rate ratio will then vary with the degree of quenching. A previous calibration is necessary to interprete the channel ratio data but once this is available the quenching assessment and the actual count can be carried out without disturbance of the vial. Unlike the methods previously described the channel ratio method does correct for total quenching including optical quenching.

A coincidence method uses three photomultipliers to view the counting vial. Two of these are connected in coincidence and the output from this is in coincidence with the third (figure 7). If n_2 and n_3 are count rates at the outputs from the first and second coincidence circuits and η is the counting efficiency of a single photomultiplier

FIGURE 7

THREEFOLD COINCIDENCE METHOD FOR
DETERMINATION OF EFFICIENCY

(SCHWERDTEL [144] 1966)

PRE-AMP.

HIGH VOLTAGE

P.M.

HIGH VOLTAGE

VIAL

HIGH VOLTAGE

P.M.   P.M.

PRE-AMP.   PRE-AMP

AMPLIFIER   AMPLIFIER   AMPLIFIER

PULSE HEIGHT ANALYSER (WIDE GATE)   PULSE HEIGHT ANALYSER (WIDE GATE)   PULSE HEIGHT ANALYSER (WIDE GATE)

COINCIDENCE CIRCUIT

COINCIDENCE CIRCUIT

SCALER $n_2 = \eta^2 n$ SCALER $n_3 = \eta^3 n$
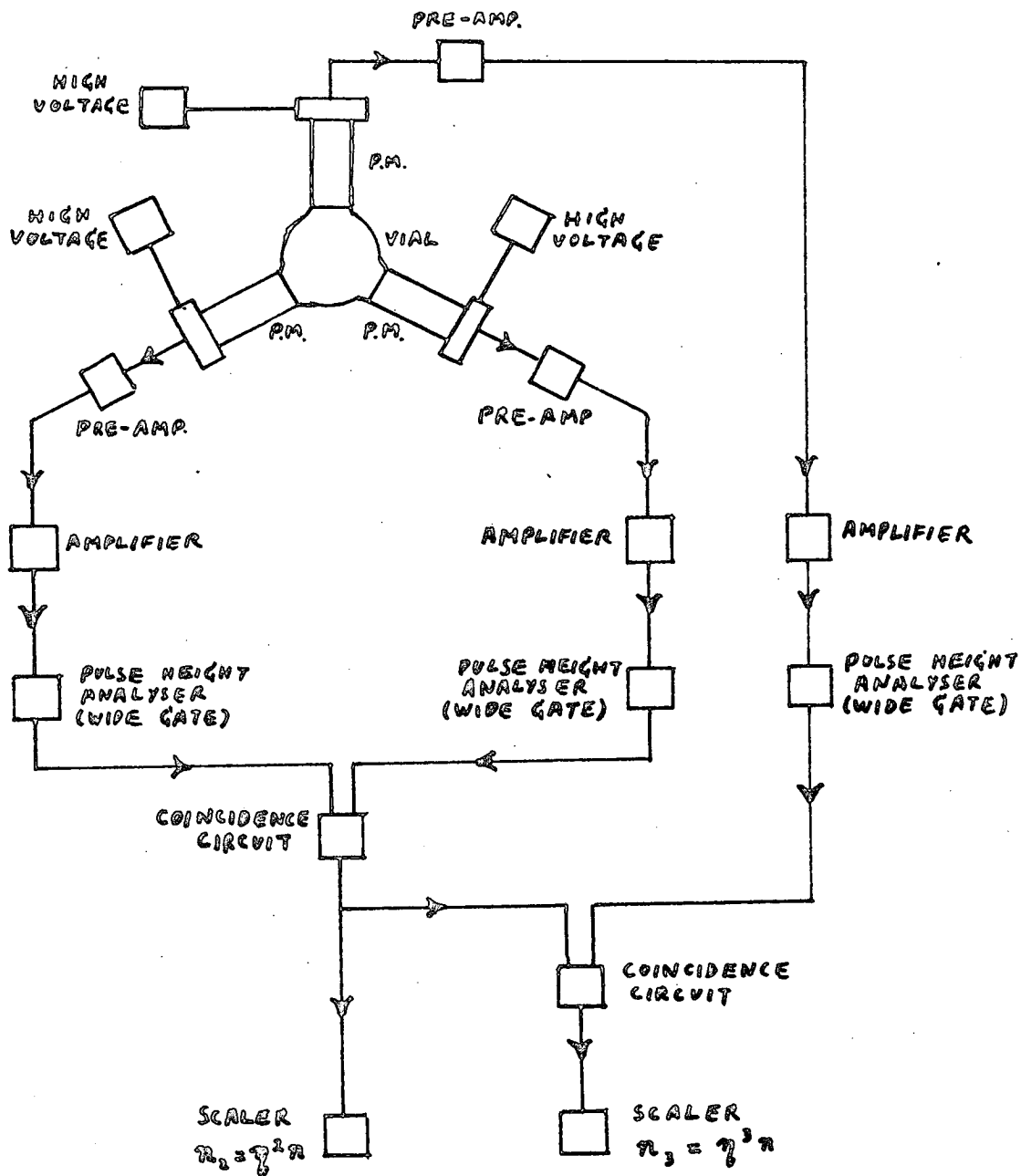
$$EFFICIENCY = \eta = n_3 / n_2$$

$$ACTIVITY = n = n_2^3 / n_3^2$$

then

$$n_2 = n\eta^2$$

and

$$n_3 = n\eta^3$$

where n is the absolute count rate of the sample. Hence a measurement of the ratio n_3/n_2 will give the efficiency η. In practice a preliminary calibration would usually be desirable.

Quenching correction can also be achieved by the use of an external standard. The standard may be introduced into the vial in the form of a sealed ampoule or needle or simply placed adjacent to it in a position of fixed geometry. In both cases the sample is not effected and may be stored for subsequent re-use. A calibration is, however, essential with the external standard method.

Counting using the external standard system may be by either single channel or channel ratio method. The single channel method is simpler but is sensitive to the geometry of the system. Thus errors will be introduced by variations in the position of the standard, vial position, vial shape and so on. The channel ratio method which requires a fixed spectral shape rather than a fixed source strength is much less sensitive to these factors. The channel ratio method is usually the preferred system for automatic systems.

Separation of colour and chemical quenching is possible using a system proposed by Ross[101]. Two separate standards in sealed ampoules for insertion in the vial are used. One contains an external standard and measures the total quenching in the usual way. The other contains a soft beta emitter (^{14}C) in a scintillator mix and acts as a source of fluorescent light only. This standard therefore measures colour

quenching only and in conjunction with the earlier measurement the chemical quenching can be calculated.

2.5 Incorporation of Radiocarbon into the Scintillator [102,103]

Homogeneous Samples

The most convenient form for the recovery of radiocarbon from the specimen is carbon dioxide, which can be obtained from biological materials by combustion in oxygen and from inorganic materials by use of acid. In fact the production of carbon dioxide is usually the first stage in the synthesis of most of the other carbon compounds which may be required. It is therefore extremely desirable from the point of view of simplicity and convenience to have a method of incorporating carbon dioxide directly into the scintillator.

The simplest method is simply to absorb the gaseous CO_2 in the toluene solvent and this was investigated by Williams in 1952[104]. He found that this was indeed possible but that the amount of carbon that could be introduced was only about 2 mg per ml scintillator at N.T.P. and 10 mg per ml at $-80^{\circ}C$, 76 cm Hg. Now it will be shown in chapter 4 that in order to achieve radiocarbon dates of the order of 50,000 years, and assuming that care has been taken to reduce the background count rate to a minimum, that at least 70 mg/ml carbon must be used. Hence direct absorption of gaseous CO_2 in toluene is not feasible for radiocarbon dating at the older end of the scale. This, of course, does not preclude the use of this technique for dating of younger objects and for radiocarbon tracer experiments.

Such a system is described by Horrocks[105] who prepared sealed vials

containing up to 2 mg carbon/ml in line with Williams results.

Barendsen 1957[106] showed that large amounts of liquid CO_2 could

be added to toluene at low temperatures and high pressures. Since his

process involved sealing the vial at liquid air temperatures and then

heating to -20^oC for counting a pressure of nearly 20 atmospheres in

the vial was reached. His experiments showed that the introduction

of the liquid CO_2 diluent did cause quenching and that this would be

the limiting factor. However, quantities of up to 70 mg/ml were

feasible and hence this method should be capable of achieving dates

of up to 50,000 years. Barendsen's apparatus was itself capable of

reaching 32,000 years.

An alternative approach is to absorb the gaseous CO_2 in a liquid

which is then added to scintillator. Such a liquid should have high

solubility for CO_2 but should not significantly quench the scintillator.

A number of suitable liquids are available such as hyamine, primene,

2-phenylethylamine etc. Results for primene[107] show that when

quenching is taken into account the amount of carbon which can be

introduced is limited to some 4 mg/ml and there is no reason to suppose

that the other liquids would be significantly better. Thus this method

is also not feasible for dating.

If the difficulty and inconvenience of chemical synthesis of

organic compounds is accepted then it becomes possible to introduce

large quantities of carbon into the scintillator. The synthesis can

lead to either a compound which is compatable with the scintillator and

causes little quenching, or to the actual scintillator solvent itself.

This latter case will obviously permit the introduction of the largest

amounts of carbon and should achieve the oldest dates.

Compounds which have been synthesised for this purpose are ethanol[73],

methanol[108], toluene[109], methyl borate[109], paraldehyde[110], benzoic acid[111]

and benzene[112-116]. Toluene would, on first appearance, appear to be the

most promising material but difficulties in the synthesis have led to

the development of the benzene method by Tamers in preference. In

Tamers method the scintillator solvent consists of 3 parts benzene to

1 part toluene. The toluene is not strictly necessary but it does permit

the scintillator and shifter to be measured out and dissolved in the

toluene previous to the experiment.

In any of these syntheses the possibility of isotopic separation

of the ^{14}C and ^{12}C must be accepted. Tamers estimates that errors

arising from this cause in the benzene synthesis are not greater than

1% and that this can be safely ignored for the older samples. For more

recent specimens this could introduce a significant error and an

estimate of the isotopic ratio must be made. In practice the $^{13}C/^{12}C$

ratio is measured by mass spectrometry and the $^{14}C/^{12}C$ ratio calculated

from this.

2.6   Incorporation of Radiocarbon into the Scintillator

Heterogeneous System

The difficulties encountered in converting the ^{14}C labelled compounds

into a form soluble in or miscible with the scintillator have led to the

development of various heterogeneous systems[117]. These should permit

the examination of the source material either directly or with a minimum

of chemical pre-treatment. The efficiency will in general be somewhat lower than the best homogeneous systems. The application to dating will therefore be to routine measurements on specimens which have originated at the more recent end of the time scale.

Heterogeneous samples have been prepared as suspensions, gels, emulsions or by the immersion of impregnated glass fibre discs in the scintillator. The most common form used for the introduction of the ^{14}C is barium carbonate, $BaCO_3$ [118,119]. This is readily prepared by first absorbing CO_2 in caustic soda NaOH and adding $BaCl_2$ to precipitate the $BaCO_3$. Some work has also been done with sodium carbonate[120,121] and with various organic materials.

All heterogeneous systems will suffer from self-absorption losses and these must be either determined or controlled. Particle size and structure will therefore be important and may have to be controlled for consistent results. For barium carbonate Cluley[118] has shown that contrary to expectations particle size does not affect efficiency, and it is surmised that the crystals of this material are composed of small units of regular size which are surrounded by the scintillator whatever the apparent size of the crystal. Other materials presumably also possess this property but no search seems to have been made for them.

Suspension counting where the source material has merely to be shaken into the scintillator is the simplest to perform. However, settling of the suspension after agitation will gradually reduce the counting efficiency. Use of a small particle size will increase the time in suspension but uncertainties about the efficiency will persist.

Correction for settling can be made by taking counts for a series of sedimentation times and extrapolating back to zero[122,123]. This procedure would obviously not be suitable for low specific activities where long count times are necessary.

Stabilisation of the suspension by use of a gelling agent will remove this sedimentation problem at the expense of some efficiency and inconvenience. Early gelling agents such as aluminium stearate required heat treatment to produce the gel but these have now been superceded by proprietary materials such as Thixcin (derived from castor oil), Cab-o-sil, and Aerosil which merely require thorough dispersion in the scintillator.

Cab-o-sil and Aerosil have been used most frequently and consist of a very finely divided silica powder. When this is dispersed in a liquid system the long chain like formations of the particles link together to form a network type of structure. Provided sufficient particles are present a thixotropic gel is formed. Upon agitation the network structure breaks up and the material becomes liquid again to reform as a gel when agitation stops. The makers of Cab-o-sil claim that 1% to 3% Cab-o-sil in toluene is sufficient to form a gel[124], however, various experimenters have found it desirable to use slightly higher concentrations as shown in table 1. The value used in the current work (chapter 6) was 4.5%.

There seems little to choose between Cab-o-sil and Aerosil as far as counting efficiency is concerned, however Koniger and Suss report a large difference with respect to phosphorescence due to absorption of light during preparation.

TABLE 1

Concentrations of Silica-gel used by various experimenters

Experimenter	Date	Application	Percentage Silica weight/vol
Cluley[118]	1962	$Ba^{14}CO_3$	4.0
Gilly and Bisci[119]	1963	$Ba^{14}CO_3$	4.0
Page, Sims and Bingham[122]	1964	Clay and Soil labelled with ^{14}C	5.0
Bull[123]	1968	(^{14}C) Melanin	4.0
Koniger and Suss[121]	1968	$Na^{14}CO_3$	4.5

Counting efficiency must be expected to decrease with the use of an excessive amount of silica but this does not appear to be critical. Koniger and Suss report that significant decrease did not take place until concentrations in the region of 8 to 9% were reached.

Emulsion or two phase systems were originally developed for counting of aqueous samples by dispersion of the water in the scintillator by use of a detergent. Self absorption will still be present but may be small if size of the water droplets are small. The favoured detergent has been Triton X-100 although a range of other suitable materials has been examined by Lieberman and Moghissi[125]. Efficiencies in the range 73-85% have been achieved for ^{14}C[126] but careful control of experimental conditions is required.

CHAPTER 3

Formulae and Statistics

3.1 Calculation of Radiocarbon Ages

The activity of the carbon-14 locked within a dead specimen will decay with the usual exponential formula

$$A = A_o e^{-\frac{\log_e 2}{T} \cdot t}$$

where A, A_o are the present activity and the original activity (at death) respectively,

T is the half-life

and t is the elapsed time since death (age).

Hence the age of the specimen is given by

$$t = \frac{T}{\log_e 2} \log_e \frac{A_o}{A}$$

By convention the Libby value of T of 5568 years is to be used for date calculations[9] and hence

$$t = 8034 \log_e \frac{A_o}{A} \tag{1}$$

Conversion from Libby years to true years can be readily effected, if required, simply by multiplying by the ratio of true half-life to the Libby half-life. That is by 1.03.

Use of this simple formula is complicated by two factors: (1) the Suess and bomb effects which have upset the present day value of the $^{14}C/^{12}C$ ratio in the atmosphere and which make it difficult to evaluate A_o and (2) isotopic effects which arise both in the uptake of carbon to the organic material in the first place and later in the preparation of the sample for counting.

The first of these problems has been solved by the acceptance as a reference standard of a batch of oxalic acid held by the National Bureau of Standards, Washington, U.S.A. This standard has itself been subject to the Suess and bomb effects but has been calibrated against wood of known origin 19th cent. that is before the large scale burning of fossil fuels. This calibration shows that this wood has an activity of 95% of that of the Oxalic acid.

Both the oxalic acid standard measurement and the actual sample measurement will be subject to isotopic effects and corrections must be applied for both. This is done by measuring the change in the $^{13}C/^{12}C$ ratio by a mass spectrometer in the two cases. These isotopic enrichments are expressed in different form per mil of a suitable standard as shown in the formula

$$\delta^{13}C = \frac{\left(^{13}C/^{12}C_{sample} - {}^{13}C/^{12}C_{stand}\right) \times 1000}{^{13}C/^{12}C_{stand}} \qquad (2)$$

Various ^{13}C standards are held by the National Bureau of Standards but in practice results are usually expressed in terms of an earlier belemnite standard used by Craig[128] at Chicago.

Once the $\delta^{13}C$ values are known the corresponding enrichments for ^{14}C are easily calculated. As shown by Craig[127] in 1954 the enrichment factor for ^{14}C is the square of the factor for ^{13}C.

i.e. If X, Y are the abundances of ^{13}C and ^{14}C respectively then

$$\frac{Y_2}{Y_1} = \left(\frac{X_2}{X_1}\right)^2$$

Hence $1 + \frac{\delta Y}{Y} = \left(1 + \frac{\delta X}{X}\right)^2$

and $\frac{\delta Y}{Y} \stackrel{.}{=} 2\frac{\delta X}{X}$ \qquad (3)

since $\frac{\delta X}{X}$ is always very small.

The measured activity A^1 is corrected for isotopic effects as follows:-

Corrected Activity $A = A^1 \dfrac{Y_{ref}}{Y_{samp}} = A^1 / \left(1 + \dfrac{\delta Y}{Y} \right)$

$$\approx A^1 \left(1 - \dfrac{\delta Y}{Y} \right) \qquad \text{since } \dfrac{\delta Y}{y} << 1$$

$$\equiv A^1 \left(1 - 2 \dfrac{\delta X}{X} \right) \qquad \text{by (3)}$$

By combining this with (2) it can be shown that

$$A = A^1 \left[1 - \dfrac{2(\delta^{13}C_{samp} - \delta^{13}C_{ref})}{1000} \right]$$

This must be applied to both the sample material and the oxalic acid standard.

For the standard a value for $\delta^{13}C_{ref} = -19.0‰$ has been established[129] while for the sample the average value for the biosphere of $-25.0‰$ is usually taken[26].

Thus the corrected standard activity becomes

$$A_o = 0.95 \, A_{ox} \left[1 - \dfrac{2(\delta^{13}C_{ox} + 19)}{1000} \right] \qquad (4)$$

and sample activity becomes

$$A = A^1 \left[1 - \dfrac{2(\delta^{13}C_{samp} + 25)}{1000} \right] \qquad (5)$$

It is conventional to express radiocarbon measurements also in per mil difference form.[51]

Thus $\qquad \delta^{14}C = \dfrac{A^1 - A_o}{A_o} \times 1000 \qquad (6)$

The true deviation of activity of the unknown sample when account is taken of isotopic fractionisation of the sample material is then obtained by replacing A^1 in (6) by the expression for A from (5) giving[51]

$$\Delta^{14}C = \delta^{14}C - (2\delta^{13}C + 50)(1 + \dfrac{\delta^{14}C}{1000}) \qquad (7)$$

The radiocarbon age in Libby years is then calculated by substituting in (1) to get

$$t = 8034 \log_e \frac{(\Delta^{14}C + 1000)}{1000} \quad . \tag{8}$$

In this treatment it has been assumed that the value of $\delta^{13}C$ of all the samples was the same as wood, that is -25%. As techniques are refined allowing a wider range of materials to be examined and higher accuracies to be attained this assumption may no longer be valid.

It should be borne in mind also that dates arrived at by equation (8) rely on the assumption that the $^{14}C/^{12}C$ ratio in the environment has always been constant at the value existing in 1890. As discussed in chapter 1 this is not so and radiocarbon dates must be corrected to calendar dates by calibrations depending on other types of chronology.

3.2 Precision of Radiocarbon Dating[130,131,132]

Any determination of activity requires that two counts, the background and the source plus background, be made. In applications to dating the source activity is always very small and hence the two count rates will be very nearly equal.

If n_S and n_B are the count-rates for source plus background and background respectively and it is assumed that errors are due to the random nature of radiations only then Poisson statistics apply. The count rate due to the source alone is

$$n_D = n_S - n_B$$

and the standard variation of this is

$$\sigma n_D = \left[\frac{n_S}{\tau_S} + \frac{n_B}{\tau_B} \right]^{\frac{1}{2}}$$

where τ_S and τ_B are the count times for the two counts.

For optimum performance, that is minimum σn_d it can be shown[130] that

$$\frac{\tau_S}{\tau_B} = \left(\frac{n_S}{n_B} \right)^{\frac{1}{2}}$$

and since $n_S \approx n_B$ for dating applications it follows that $\tau_S = \tau_B = \frac{1}{2}\tau$, where τ = total counting time.

Two such measurements of activity are required to define a radiocarbon age by use of equation (1) which becomes

$$t = 8034 \, \log_e \frac{n_{ST} - n_B}{n_S - n_B} \tag{9}$$

where n_{ST} is the counting rate obtained using the standard material.

The standard deviation/of the age can be calculated from[131]

$$\sigma_t{}^2 = (8034)^2 \left[\left(\frac{\sigma n_S}{n_S - n_B} \right)^2 + \left(\frac{n_{ST} - n_S}{n_{ST} - n_B} \right)^2 \left(\frac{\sigma n_B}{n_S - n_B} \right)^2 \right.$$

$$\left. + \left(\frac{\sigma n_{ST}}{n_{ST} - n_B} \right)^2 \right] + \left(1.44 \sigma_T \, \log_e \frac{n_{ST} - n_B}{n_S - n_B} \right)^2 \tag{10}$$

where σ_T is the standard deviation of the half-life T.

The maximum and minimum ages which can be determined using a given set of apparatus can then be estimated from equation (9).

The maximum age is given by the smallest value of $n_S - n_B = n_D$ which can be measured with the desired degree of precision. That is the difference $n_S - n_B$ should be sufficiently great that it is unlikely that it would arise randomly by a simple repetition of the same count.

If we define $k = \dfrac{n_S - n_B}{\sigma_{n_D}}$ as the reduced deviation then the probability that the difference is significant can be evaluated as a function of k (Table 2). From the table we see that if k = 2 it is 95.5% certain that the result is significant and for k = 4, 99.99% certain.

TABLE 2

Reduced Deviation $k = \dfrac{n_D}{\sigma_{n_D}}$	Level of Significance % age
0.1	8
0.5	18.3
0.67	50
1	68.3
2	95.5
3	99.73
4	99.99

Since $n_S \approx n_B$

$$\sigma_{n_D} = \sqrt{\sigma_{n_S}^2 + \sigma_{n_B}^2} \approx \sqrt{2}\,\sigma_{n_B}^2$$

and the minimum value of $n_S - n_B$ is $k\,\sigma_{n_D} = k\,(\sqrt{2}\,\sigma_{n_B})$

Hence from equation (9)

$$t_{max} = 8034 \log_e \frac{n_{ST} - n_B}{k(\sqrt{2}\,\sigma_{n_B})} \tag{11}$$

It will be obvious that the maximum age depends on three factors:

(1) the standard deviation of the background activity

(2) the measured activity of the standard $n_{ST} - n_B$

(3) the level of significance selected (usually 95.5% or 99.99%).

The first of these must include the experimental limitations as well as the statistical effects.

The second can be increased by either increasing the amount of the standard which can be incorporated or by reducing the background count n_B.

The minimum age is calculated in a similar fashion, the requirement now being that $\dfrac{n_{ST} - n_B}{n_S - n_B}$ be significantly different from unity.

i.e. For the minimum

$$\frac{n_{ST} - n_B}{n_S - n_B} - 1 = k\sigma$$

where σ is the standard deviation of $\dfrac{n_{ST} - n_B}{n_S - n_B}$.

Using (9) this leads to

$$t_{min} = 8034 \log_e \left[1 + \frac{k\sqrt{2(\sigma_{n_{ST}}^2 + \sigma_{n_B}^2)}}{n_{ST} - n_B} \right] \qquad (12)$$

A value of $k = 1$ (68.3% significant) is usually taken for this calculation.

3.3 Factor of merit

Various low background counting assemblies may use different counting methods, accept different amounts of source material and possess different background counting-rates. Assessment of the relative performances of different systems used to count the same source material is difficult. Use may be made of counting statistics theory to indicate which factors are of importance when making comparisons.

Using the same terminology as in the last section the count-rate due to the source material is

$$n_D = n_S - n_B$$

and the standard deviation is

$$\sigma_{n_D} = \left[\frac{n_S}{\tau_S} + \frac{n_B}{\tau_B} \right]^{\frac{1}{2}}$$

The condition for optimum division of time between the background and source plus background counts is again

$$\frac{\tau_S}{\tau_B} = \left(\frac{n_S}{n_B} \right)^{\frac{1}{2}}$$

where $\tau_S + \tau_B = \tau$ = total counting time.

Substitution of $k = \frac{n_D}{\sigma_{n_D}}$ in these equations and elimination of n_S leads[130] to the relation

$$k = \frac{\sqrt{\tau}}{\frac{\sqrt{n_B}}{n_D} + \left[\left(\frac{\sqrt{n_B}}{n_D} \right)^2 + \frac{1}{n_D} \right]^{\frac{1}{2}}}$$

For very low activity sources such as are met with in radiocarbon dating it can usually be assumed that $n_D \ll n_B$ and in this case the relation reduces to

$$k \approx \frac{\sqrt{\tau}}{2\sqrt{n_B} / n_D}$$

Since a large value of k corresponds to a small value of σ_{n_D} and hence to high precision, and since k increases as $n_D/\sqrt{n_B}$ increases this group is defined as the Factor of Merit and is used in comparisons between different installations. For very low background systems it may no longer be permissible to ignore the term $\frac{1}{n_D}$ in the expression for k and hence the factor of merit has to be used with discretion.

Comparisons must be made with reference to a given radioactive species at a given specific activity. For radiocarbon dating it has been the usual practice to take n_D as the count-rate (counts per minute) obtained using a sample prepared from modern carbon. Typical values for the factor of merit for radiocarbon installations range from 1 to 100 $\min^{-\frac{1}{2}}$.

CHAPTER 4

Design of the Radiocarbon Dating Installation

4.1 Introduction

At the time this project was initiated dating systems capable of reaching to about 50,000 years were already in existence or planned[112]. These systems used the liquid scintillation method and incorporated the radiocarbon in the solvent by the synthesis of benzene. Since benzene (C_6H_6) contains 92% carbon by weight this method is undoubtedly capable of achieving the highest sensitivities and establishing the oldest dates.

The synthesis of benzene, however, requires several stages and specialised chemical equipment. Even in the streamlined system used by Tamers[113] it was necessary to go through the following stages

(a) combustion of sample in oxygen to produce carbon dioxide

(b) reaction of the carbon dioxide with molten lithium to produce lithium carbide

(c) reaction of the carbide with water to produce acetylene gas (C_2H_2)

(d) polymerisation of the acetylene to form benzene over a suitable catalyst[135].

According to Tamers this process will take at least 8 hours.

Beyond 50,000 years the benzene synthesis method is probably the only one feasible unless isotopic enrichment is carried out[115,116]. However, at these ages the problem of source integrity becomes important and great care must be exercised both in the field, when the sample is retrieved, and in the sample pre-treatment, prior to dating, to ensure
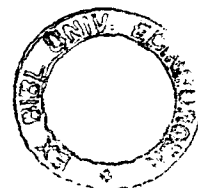
freedom from contamination from modern carbon. As discussed in chapter 1 this consideration sets an upper practical limit to radiocarbon dates of around 60,000 years.

An examination of lists of dates arrived at by radiocarbon dating shows that the bulk of the objects which a laboratory may be required to date will have originated in the period since the last ice age, that is over the last 10,000 years. A smaller number will have ages from 10,000 to 30,000 years and only a few longer than this. It follows therefore that there exists a need for a system which can carry out routine measurements over the period 0 to 30,000 years, which is more convenient to use than the benzene synthesis method, and yet which is capable, on occasion, of extension up to 50,000 years. The project reported here was an attempt to satisfy this need.

The apparatus was to be designed and installed in the Nuclear Physics laboratories of Paisley College of Technology in cooperation with the University of Edinburgh. In recognition of the requirement for convenience it was intended that all chemical operations be sufficiently straightforward so that they could be carried out on the spot in the Nuclear Physics laboratory.

The liquid scintillation method was selected in preference to the gas proportional counter because:

(a) gas proportional systems have already been highly developed and offer less scope for improvement than liquid scintillation systems,

(b)   gas proportional counters are very sensitive to the presence

of impurities and the requirement for high purity might make

it difficult to realise a simple chemical system,

(c)   some experience in liquid scintillation counting had already

been gained at Paisley.

The requirement that the radiocarbon extraction be kept simple

suggested that this be confined to a combustion system to produce

carbon dioxide and a purification train.   The problem of introducing

carbon dioxide into the scintillator, in sufficient quantities to

achieve the older dates, has   already been discussed in sections 2.5

and 2.6.   The only feasible method appears to be that due to Barendsen

1957[106] who dissolved the carbon dioxide into a toluene based

scintillator at low temperature and high pressure.   Since the liquid

air needed to carry out this process was available in quantity at

Paisley it was decided to adopt Barendsen's method in principle and

attempt to develop it so that dates of 50,000 years were possible.

The capability of Barendsen's apparatus was 32,000 years.

Barendsen's equipment consisted of a 75 ml pyrex vial viewed by

two photomultipliers in coincidence, as in Arnolds experiment, so as

to reduce the number of spurious pulses due to dark current.   The

shielding consisted of four inches of iron and half inch of lead.

Possible improvements are:

(a)   increase in vial size to increase the amount of carbon present,

(b)   use of a quartz vial to reduce background,

(c)   use of an anticoincidence shield as in the experiments of Libby[50]

or Nygaard[133].

(d)   improvement of the shielding (Delaney[134])

In the new installation it was decided to follow up all of these possibilities.

4.2   The Sample Vial

The extension of Barendsen's method to greater ages requires both the reduction of the background and the increase of the sample count. The latter aim can only be achieved by increasing the cell volume, since Barendsen had already noted that increasing the percentage of carbon dioxide above some 35% resulted in an unacceptable degree of quenching. The problem therefore was to decide what size or sizes of vials would be necessary to cover the range 0 - 50,000 years assuming that all the steps outlined in the previous section were taken to reduce the background.

It was not possible to predict the background level which might be achieved as no exactly similar arrangement had been tested. However, by consideration of the experimental results listed in table 3 it was decided that a background of 15 d min^{-1} was a reasonable design figure. At the time of this decision Arslanov's results, which show the effect of increasing the vial volume, were not available. These results are plotted in figure 8 and show that for Arslanov's arrangement a background of 18 d min^{-1} would have been expected for a vial of the same size as finally decided on here.   Since Arslanov did not use anti-coincidence shielding the figure of 15 d min^{-1} previously selected does not seem unduly optimistic.

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Table 3

Background Count-rates of Liquid Scintillation Radiocarbon Installations

Investigator	Date	Vial Size (ml)	Background (d min^{-1})	Comments
Pringle[108]	1955	20	3.3	Single Channel Pb-Hg Shield
Barendsen[106]	1957	75	13.5	Two Channel Fe-Pb Shield
Delaney[134]	1959	50	13.6	Two Channel Fe Shield
Tamers[112]	1960	20	13	Two Channel
Nyg'aard[133]	1961	100	51	Two Channel Fe Shield
			16	Anti-coinc Shield
Arslanov[116]	1968	33.56	6.6	Two Channel Fe-Hg Shield
		89.70	12.4	
		169.7	16.0	

FIGURE 8

BACKGROUND COUNT-RATE AGAINST VIAL VOLUME

(EXPERIMENTAL RESULTS BY ARSLANOV ET AL 1968 [116])
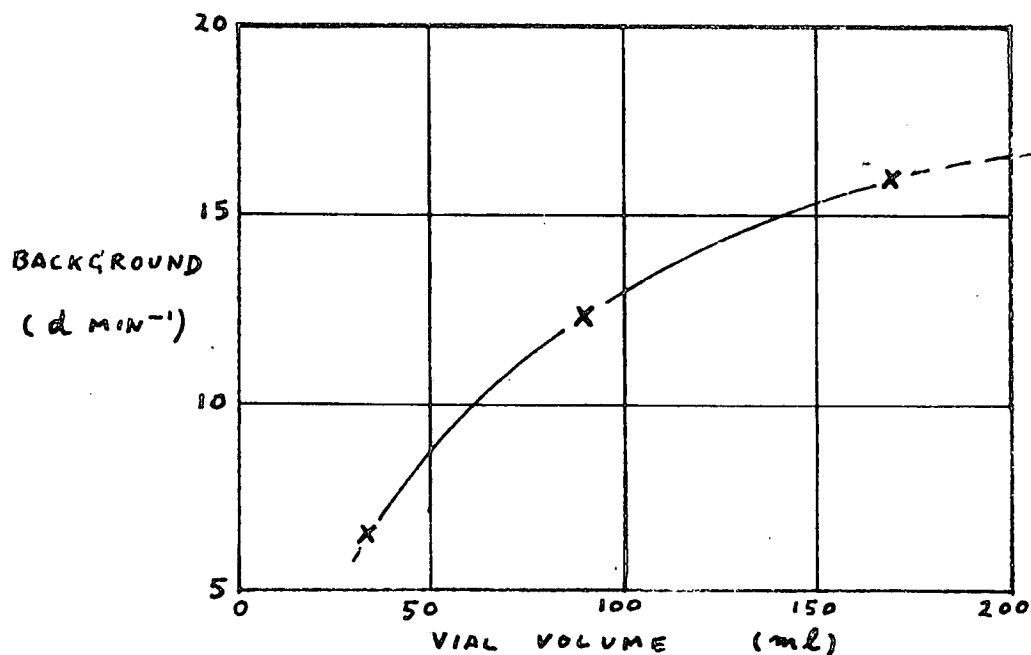
The maximum carbon dioxide concentration in the scintillator was taken as 30% by weight as recommended by Barendsen which along with the specific gravity of toluene (0.87) gave the relation between the volume, V (ml), of the scintillator and the mass, M (g), of labelled carbon incorporated in it.

$$M = 0.071 \ V \qquad\qquad (13)$$

Other design data were:

Specific Activity of Modern Carbon $= 15 \ d \ min^{-1} \ g^{-1}$ (Leger[58])

Maximum Age $= 9$ half-lives

$= 50,112$ years Libby

Maximum Count Time $= 48$ hours

The level of precision was that given by the $4 \ \sigma$ criterion (k = 4) as recommended by Crevecoeur[131].

These data were substituted into equation 11 of chapter 3 to give a mass of carbon of 14 g. From equation 13 the minimum vial volume was therefore 200 ml.

As a 200 ml vial would require considerable care in handling and as most of the dates required would be less than 30,000 years it was judged convenient to obtain in addition a smaller vial for routine work. This was chosen arbitarily to have a volume of 32 ml.

The limiting performances of the two vials were calculated using equations 11 and 12 of chapter 3 and are shown in figure 9. For the minimum ages a 68.3% level of precision (k = 1) was used following Crevecoeur. From the figure it can be seen that the larger vial even with a relatively low count time of 4 hours would achieve ages of the

FIGURE 9

LIMITATIONS TO THE AGES WHICH MAY BE DETERMINED USING THE TWO SAMPLE VIALS. (CALCULATED)
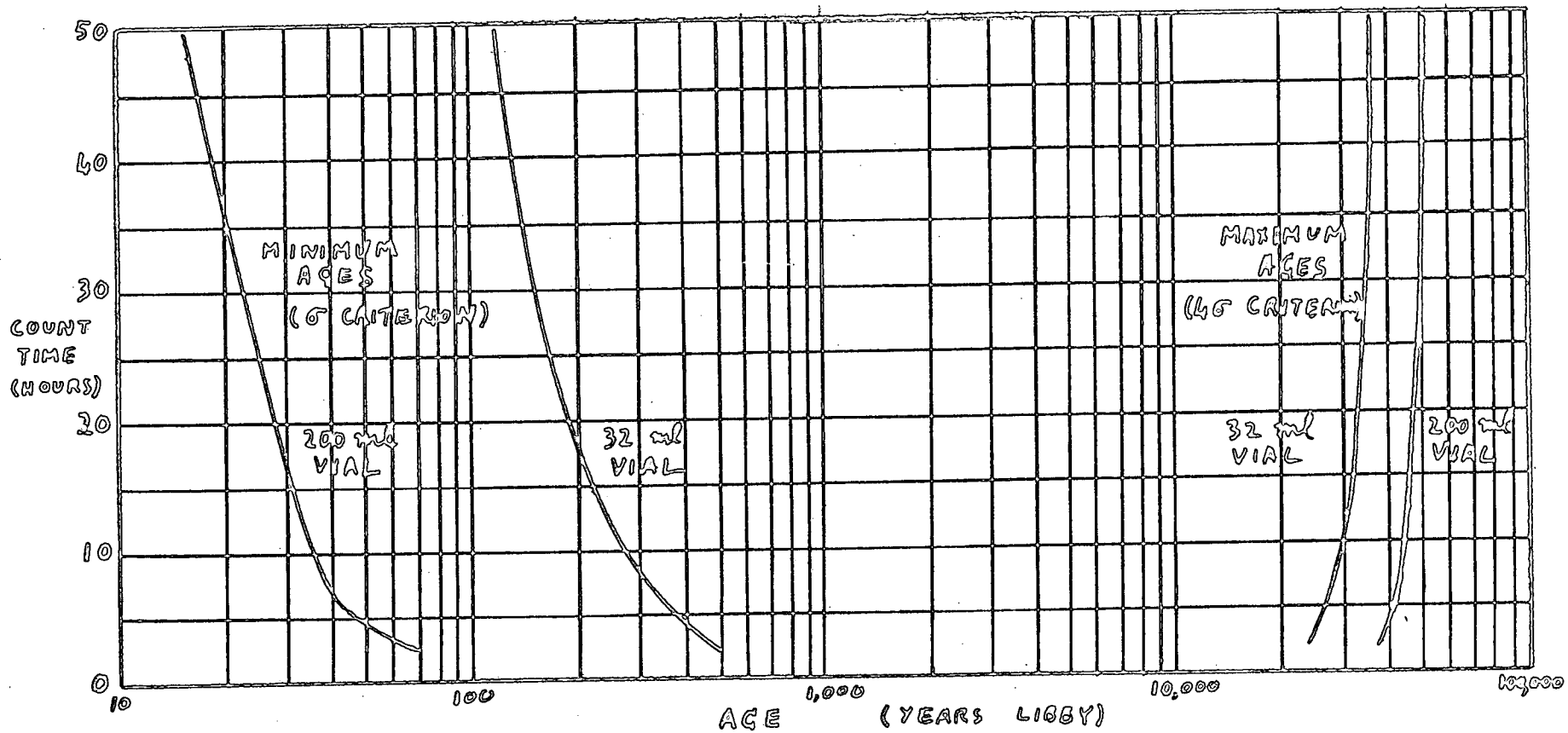
order of 40,000 years. The smaller vial although slightly more limited

for recent samples could be used for ages of up to 25,000 to 35,000

years with count times of 4 to 48 hours.

The effect of an increase in background count rate from 15 d min^{-1}

to 20 d min^{-1} would be to reduce the maximum age to 48,900 years Libby

(about 50,000 calendar years). The effects of reduced counting

efficiency are more serious, an efficiency of 50% reducing the maximum

age to 46,500 years Libby (about 47,600 calendar years).

Apart from the vial size there was a possibility that shape might

be important. In Barendsen's apparatus a cylindrical form was used

with the two photomultipliers viewing opposite ends. The contribution

to the background of optical feedback from one photomultiplier to the

other was shown to be less than 1 count per minute by Delaney and

McGovern[136] and accordingly this factor was ignored and the convenient

end to end viewing arrangement retained.

The decision to use titanium dioxide as a reflective coating was

based on a report by Cummins, Delaney and McAulay[137] that such a

coating raised the counting efficiency to 1.19 times that of an

uncoated vial.

Finally the mechanical strength of the vial had to be considered.

Since the vial would be filled and sealed at liquid air temperatures

and then raised to $-20^{\circ}C$ for counting the pressures developed would be

considerable. Calculations were performed assuming that a small quantity

of nitrogen remained above the scintillator at time of sealing to act

as a cushion as the temperature rose. The specific gravity of solid

toluene at liquid air temperatures was determined as 1.16 by a subsidiary

experiment and other data were obtained from tables. It was found

for the large vial that with a free space of 15 ml above the

scintillator, measured at room temperature and pressure, that after

sealing the pressure would rise to 11.8 atmospheres at $-20^{\circ}C$ and 12.8

atmospheres at $+20^{\circ}C$ in the event of a failure of the cooling system.

For the same pressures a free space of 2.5 ml approximately was

required with the small vial. From safety considerations a design

pressure of 25 atmospheres was used and the stopper retaining springs

were selected to release the pressure between 15 to 17 atmospheres.

After consultation with the makers, Heraeus of Sweden, a wall

thickness of 5 mm was used and the quartz vials were constructed to

the dimensions shown in figure 10.

4.3 Shielding and Cooling System

The cell containing the vial and photomultipliers is shown in

figure 11. Shielding in all directions was provided by 100 mm thick,

aged lead plus antimony bricks with curved mating faces, supplied by

Associated Lead Manufacturers Ltd. The inside walls of the cell were

lined with cadmium sheet (0.75 mm thick) and then copper sheet

(0.32 mm thick) to reduce the background due to the fluorescent X-rays

produced in the lead. The fluorescent X-rays produced finally in the

copper are of energy 8 kev and should not be detected. A special

adhesive, Evo-stik 561.D, selected because it apparently contained no

materials likely to add to the background count, was used. Finally

the cell was lined, internally with 20 mm thick expanded polystyrene

sheet to act as a thermal insulation.

PLATE 1
SAMPLE VIAL

FIGURE 10
SAMPLE VIAL

DIMENSIONS OF SMALLER VIAL IN BRACKETS

MAX. PRESSURE = 25 ATMOSPHERES
WALL THICKNESS = 5 mm
MATERIAL - QUARTZ

CONICAL
SOCKET
TYPE B 5/13
(BS 572)

FLAT
END
FACE

51 mm O.D.
(45 mm)

FLAT
END
FACE

100 mm
(90 mm)

100 mm (46 mm)
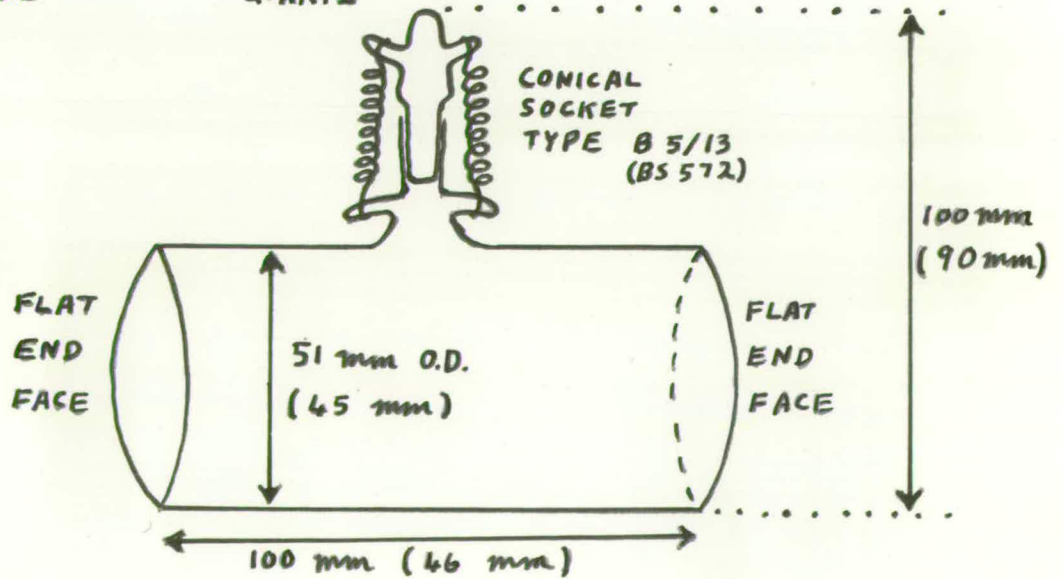
FIGURE II
THE COUNTING CELL

MATERIAL — AGED LEAD WITH 4% ANTIMONY ADDED
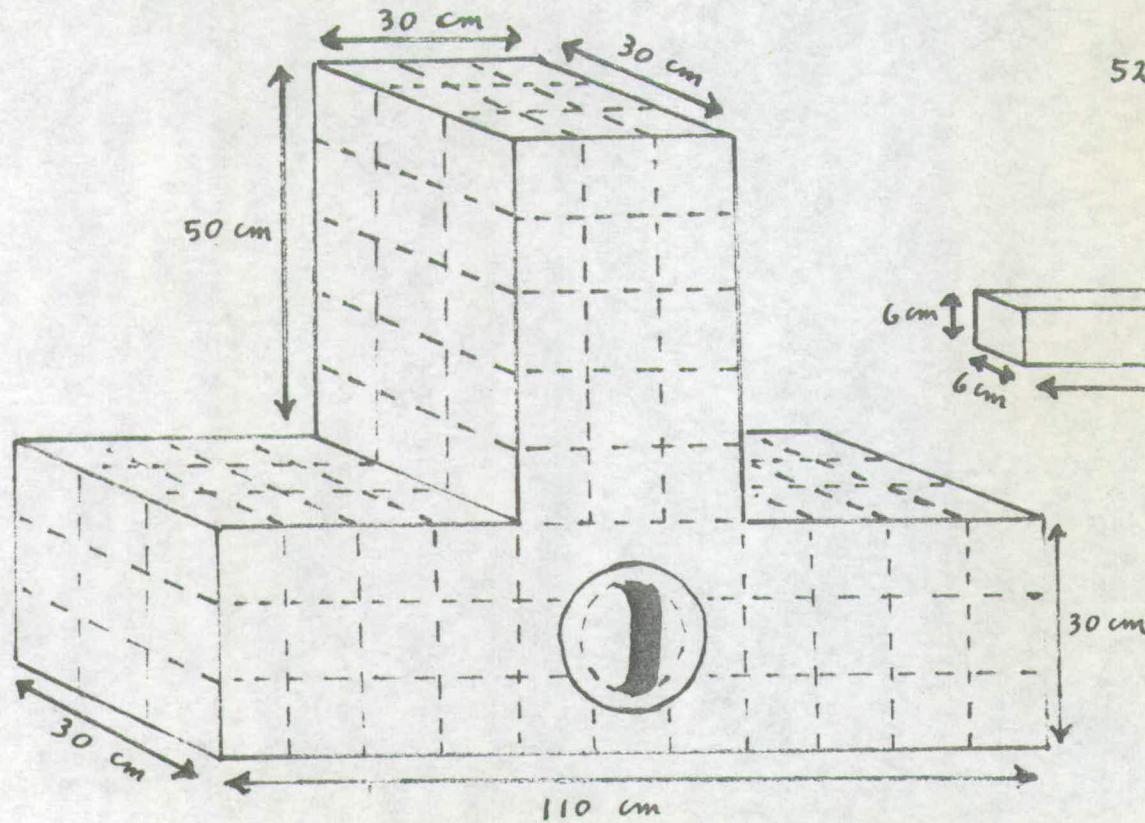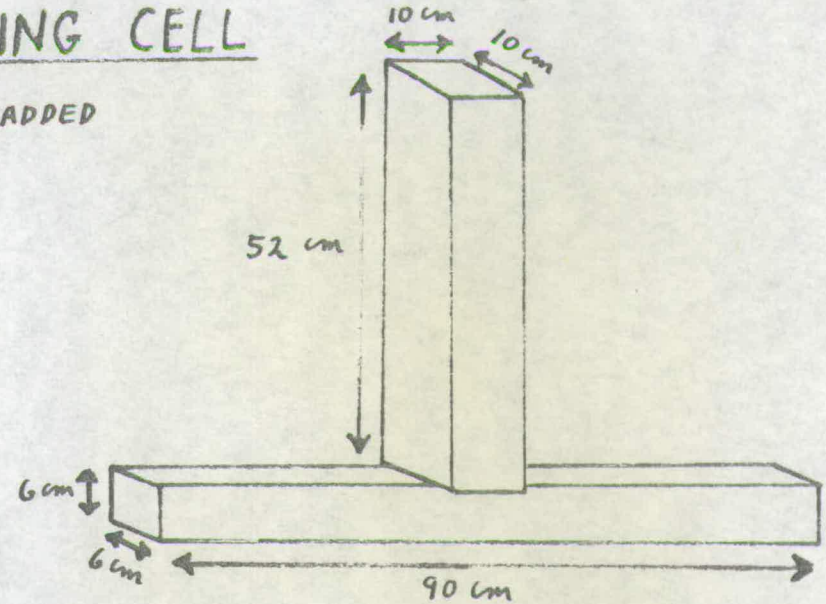
INTERNAL DIMENSIONS

(ONLY THE LOWER PART OF THE CELL IS LINED WITH THERMAL INSULATION)

EXTERNAL DIMENSIONS

PLATE 2
COUNTING CELL
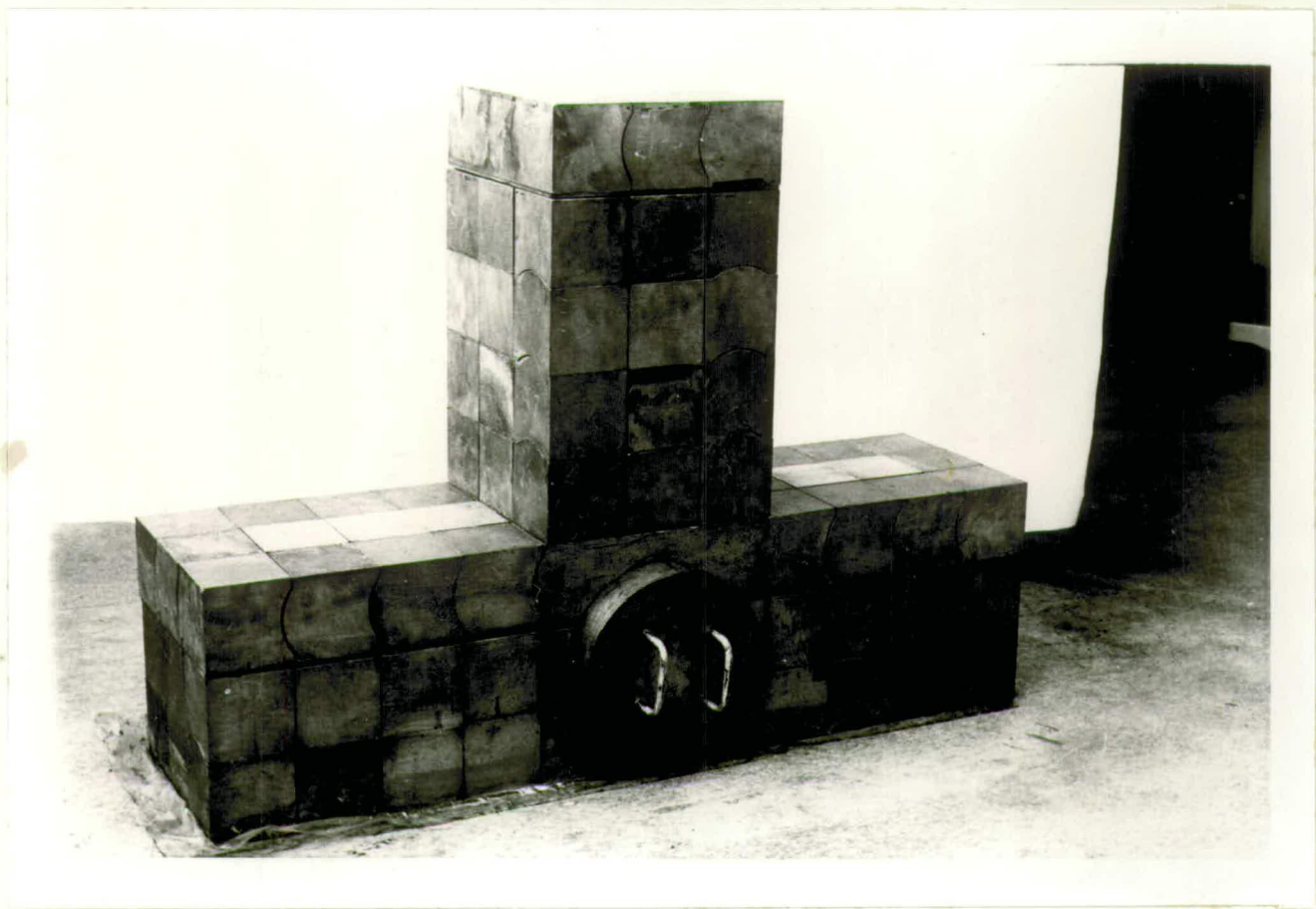
Cooling was provided by a flow of cold dry air injected just above the vial and allowed to escape via the cracks between the bricks. The cold air was evolved from a supply of liquid air by means of a small nichrome heating coil (27Ω) which was controlled by a thermostatic regulator with sensitive element placed close to the vial. The low voltage required for the heater was obtained from a variable transformer. In addition to the thermostatic control three chromal-alumal thermo-couples were included to monitor the temperature.

The anti-coincidence shielding, contained in the vertical section of the cell, consisted of a 12 mm thick, 95 mm square plastic scintillator (NE102A) connected by a conical perspex light pipe to the photomultiplier. The outer surfaces of the scintillator and light pipe were coated with titanium dioxide as a light reflector.

4.4 Electronics

The basic circuit is shown in block diagram form in figure 12.

The input pulses from the preamplifiers are amplified by some 5 times in the case of the count channels and 10 times in the anti-coincidence channel. Timing signals are taken from each amplifier to cross over pick-off circuits, so as to give sharply defined timing pulses which are used to operate the coincidence and anti-coincidence gates. The output from the anti-coincidence gate is used to operate two linear gates in each of the counting channels. The signals to be counted are taken directly from the amplifier output, added to a fixed 50 mV level provided by a monostable pulse generator activated by the output pulse itself, delayed and passed to the linear gates.

FIGURE 12

BLOCK DIAGRAM OF PRIMARY ELECTRONIC SYSTEM
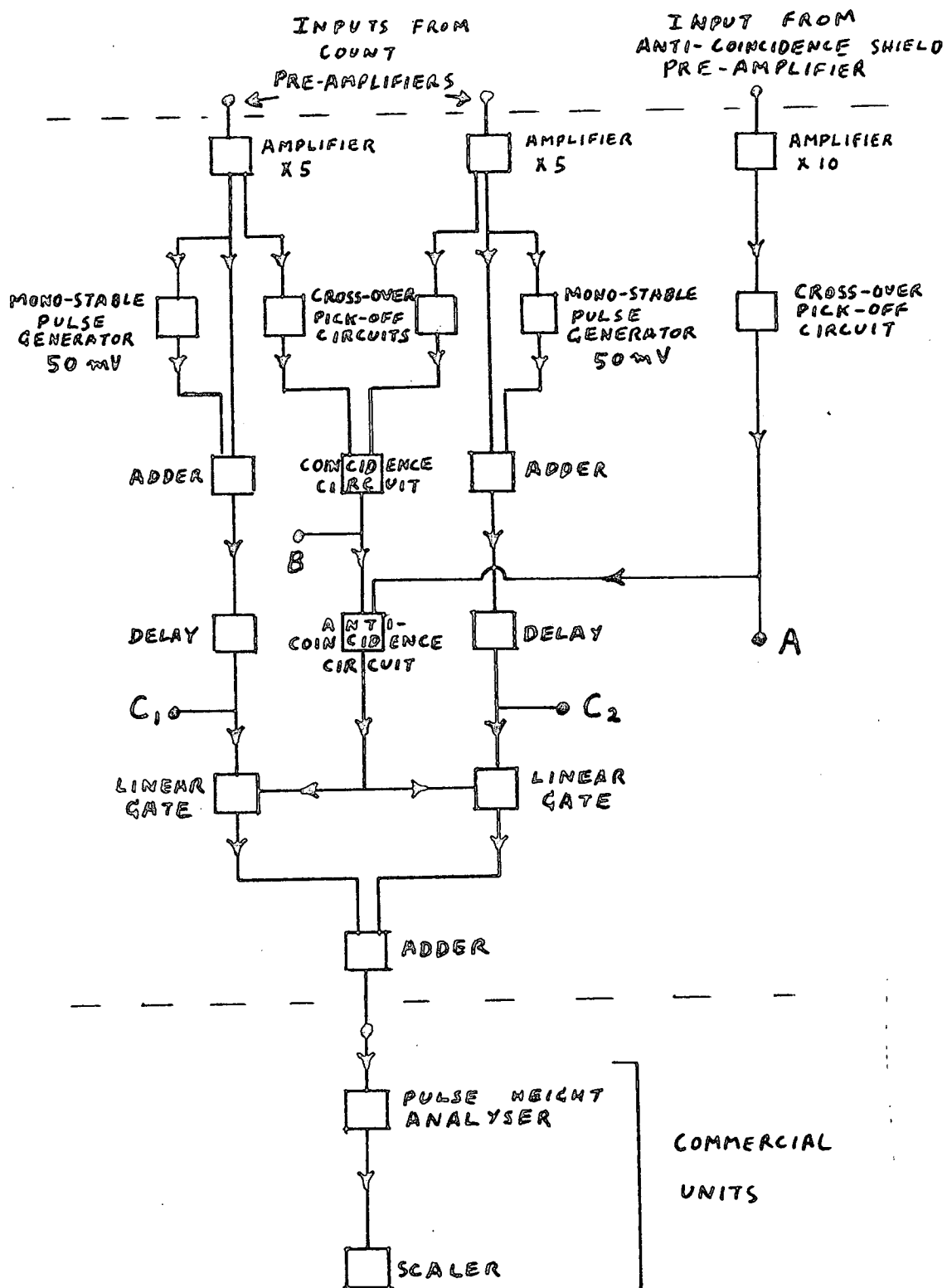
The 50 mV shift of zero serves to expand the spectrum of the radio-carbon within the counting window. After passing the gates the output is fed to a conventional system consisting of pulse height analyser and scaler. Additional outputs, A, B, C, are provided as indicated to provide a check on the operation of the equipment.

The subsidiary circuits used to check the equipment are shown in figure 13. The various outputs give:

A. Count from the anti-coincidence detector.

B. Count in the selected counting window without the use of the anti-coincidence shield.

C. Count above the counting window.

These counts in conjunction with the principal count in the window with anti-coincidence screening, permit checks to be made of the total cosmic ray background which should vary with atmospheric pressure, and of the ratio of this background in the window to the background above the window which should remain constant. Since all four counts could be taken simultaneously it should be possible to pick out and reject any run which coincided with a high cosmic ray flux or with a fault on the electronics.

The photomultipliers used were EMI type 6097S selected for low dark current and were enclosed in μ-metal screens. The dynode chain, figure 14, and pre-amplifier (Nuclear Enterprises NE5281) were encapsulated in a semi-rigid silicon gel. This was successful in preventing condensation and protecting the circuit but made it very difficult to carry out modifications or repairs. At a later stage the silicon encapsulation was replaced by a sealed perspex box which

FIGURE 13

BLOCK DIAGRAM OF SECONDARY ELECTRONIC SYSTEMS

OUTPUTS FROM PRIMARY CIRCUIT (FIGURE 12)

A B C_1 C_2

ADDER

LINEAR GATE

PULSE HEIGHT ANALYSER

WITHIN COUNT WINDOW

ABOVE UPPER DISCRIMINATOR

DRIVING AMPLIFIER

DRIVING AMPLIFIER

DRIVING AMPLIFIER

SCALER

SCALER

SCALER

COINCIDENCE CIRCUIT

POSSIBLE FUTURE DEVELOPMENT

SCALER
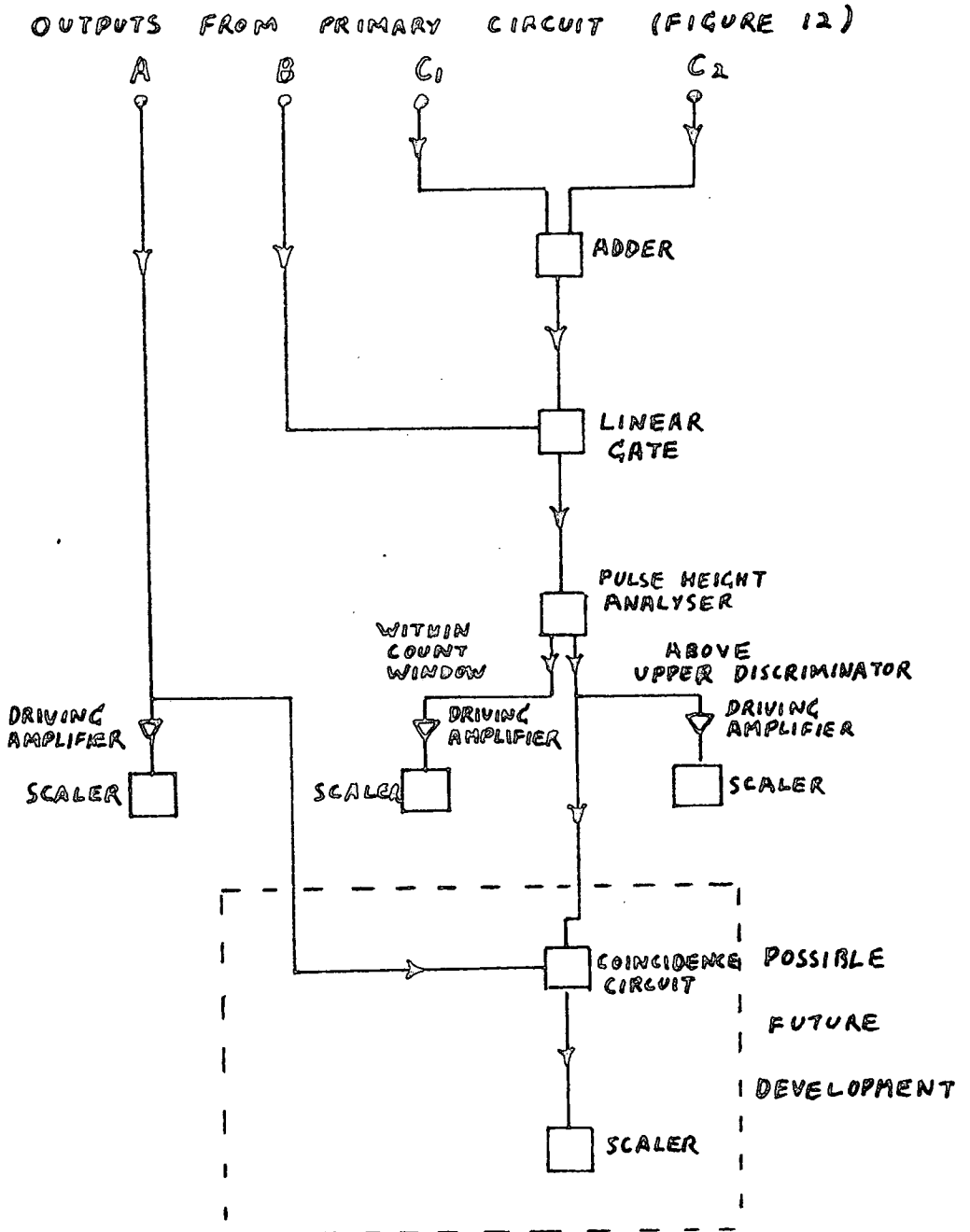
FIGURE 14
PHOTOMULTIPLIER DYNODE CHAIN

PHOTOMULTIPLIER E.M.I. 6097 S

HIGH VOLTAGE
(DESIGN VALUE 1120V)
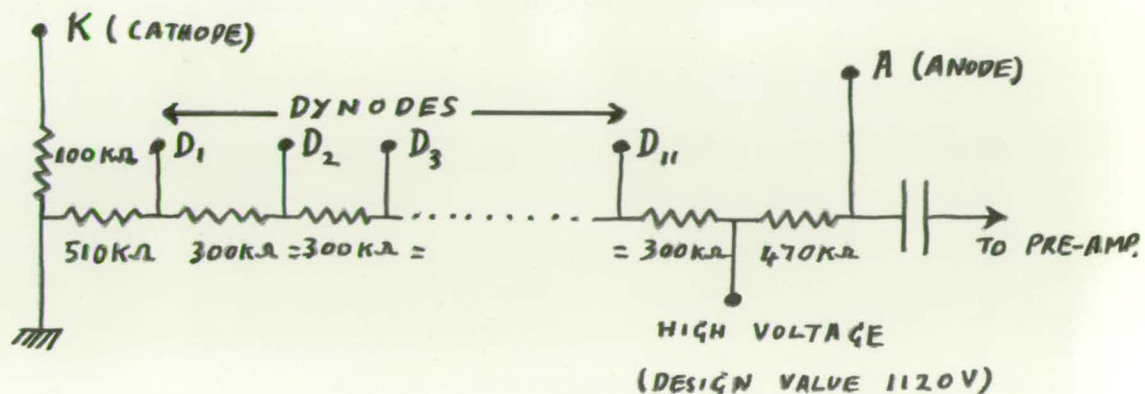
PLATE 3
PHOTOMULTIPLIER PRE-AMPLIFIER ASSEMBLY
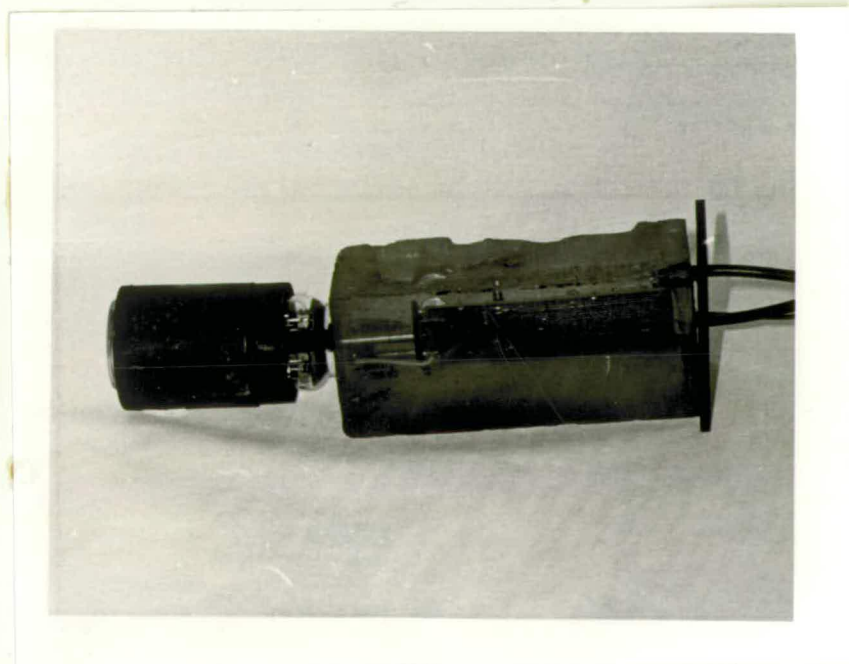
PLATE 4
ELECTRONICS
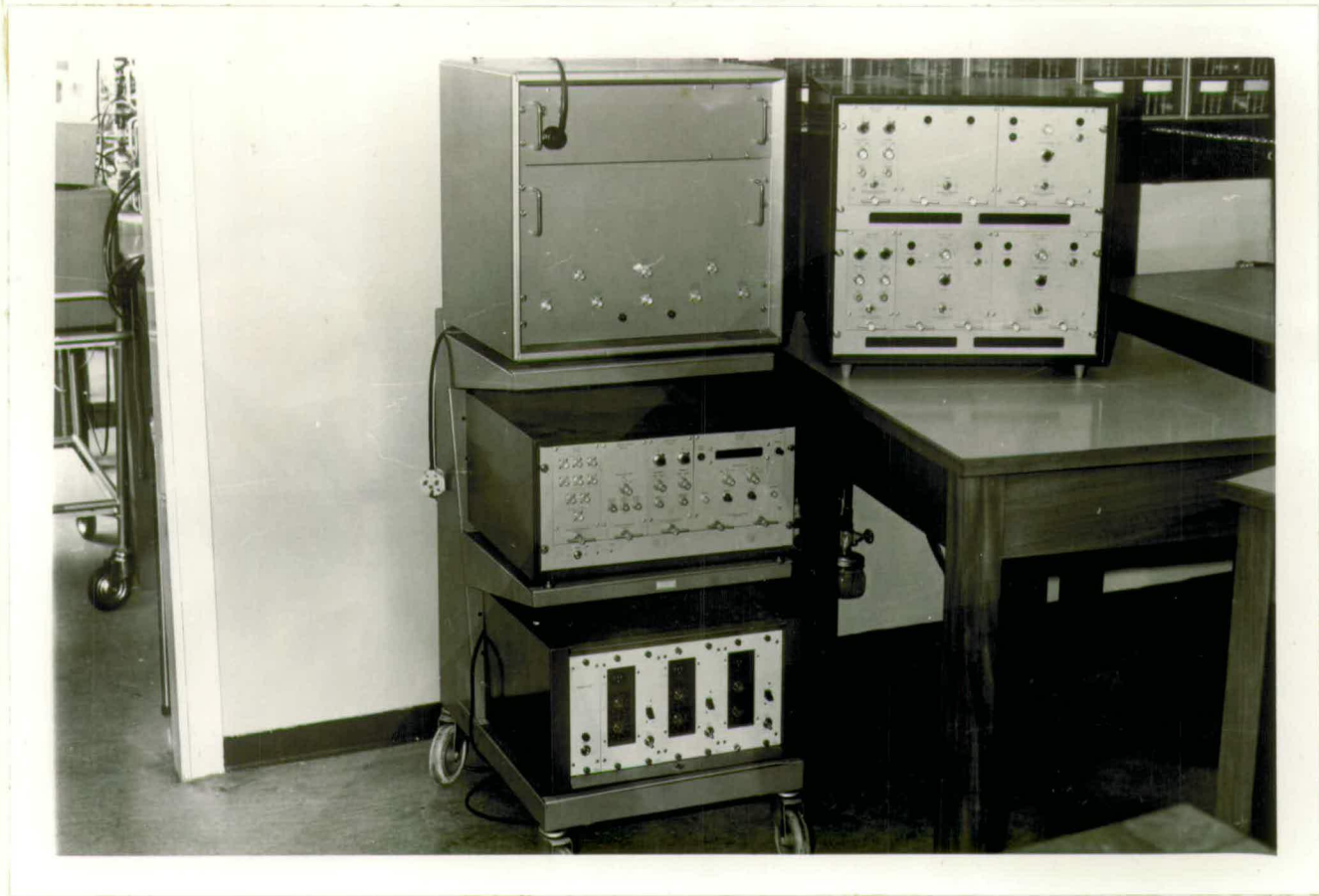
proved adequate in preventing condensation and gave easier access.

All of the amplifier, coincidence, gating and adding circuits were constructed in the Electronics workshop of the Physics Department at Paisley. Most of the circuits were taken with slight modifications from a paper by Kootsey[138]. The linear gates followed the design of Elad and Rozen[139]. Most of the modifications were concerned with the matching of different parts of the circuit. Considerable trouble was experienced with pick-up both electro-magnetically and along the power lines and extensive screening was required.

The remainder of the electronics were commercial units from the Edinburgh series of Nuclear Enterprises Ltd. with the exception of the three scalers used for checking purposes which were from Panax Ltd.

In addition there became available later a ratemeter, pen-recorder spectrometer system with automatic sweep and a Laben 400 channel analyser. These instruments were useful for setting up purposes.

A general discussion of electronics and liquid scintillation counting is given by Price[140].

4.5 <u>Production of Carbon Dioxide and its Incorporation in the Sample Vial</u>

The method used to produce the carbon dioxide (figure 15) is essentially that described by the British Standard Institution for the analysis of coal[141]. The organic specimen is combusted at $800^{\circ}C$ in a continuous flow of air. The air was obtained from the laboratory high pressure line which is fed by a compressor situated outside the

laboratory and therefore free from possible radioactive contamination. The air was purified, dried and the carbon dioxide removed by passing it through bubblers containing sulphuric acid, potassium hydroxide and sulphuric acid in that order before entering the combustion tube. After combustion the gaseous products were passed over copper oxide at $800^\circ C$ to oxydise any carbon monoxide to carbon dioxide, over lead chromate at $600^\circ C$ to absorb oxides of sulphur and finally over silver gauze to absorb chlorine.

The emerging gas mixture will contain water, nitrogen dioxide, oxygen, nitrogen in addition to the desired carbon dioxide. The water and nitrogen dioxide were removed by passing through magnesium perchlorate and granular manganese dioxide respectively and the water evolved by the absorption of the nitrogen dioxide was absorbed in a second magnesium perchlorate absorption tube. The carbon dioxide was then trapped by a liquid oxygen cold trap and the remaining nitrogen and oxygen passed on out of the system via a sulphuric acid bubbler which acted as a flow indicator.

The sample material was introduced into the combustion tube in small pieces placed in a porcelain boat. For powdered materials such as peat it was convenient to compress the material into pellets using a pellet press.

After completion of the combustion process which took between $1\frac{1}{2}$ to 2 hours the system was flushed with nitrogen and then the cold trap was isolated from the rest of the system. Since this process gave consistent yields of the order of 100% the amount of carbon dioxide

FIGURE 15

CARBON DIOXIDE PRODUCTION

COMPRESSED AIR OR NITROGEN

SULPHURIC ACID

POTASSIUM HYDROXIDE

SULPHURIC ACID

COPPER GAUZE

SAMPLE

COPPER OXIDE

LEAD CHROMATE

SILVER GAUZE

STARTING POSITION   FINAL POSITION

FURNACE No. 1 800°C

FURNACE No. 2 800°C

FURNACE No. 3 600°C

MANGANESE DIOXIDE

MAGNESIUM PERCHLORATE

MAGNESIUM PERCHLORATE

LIQUID OXYGEN

TO COUNTING VIAL

SULPHURIC ACID
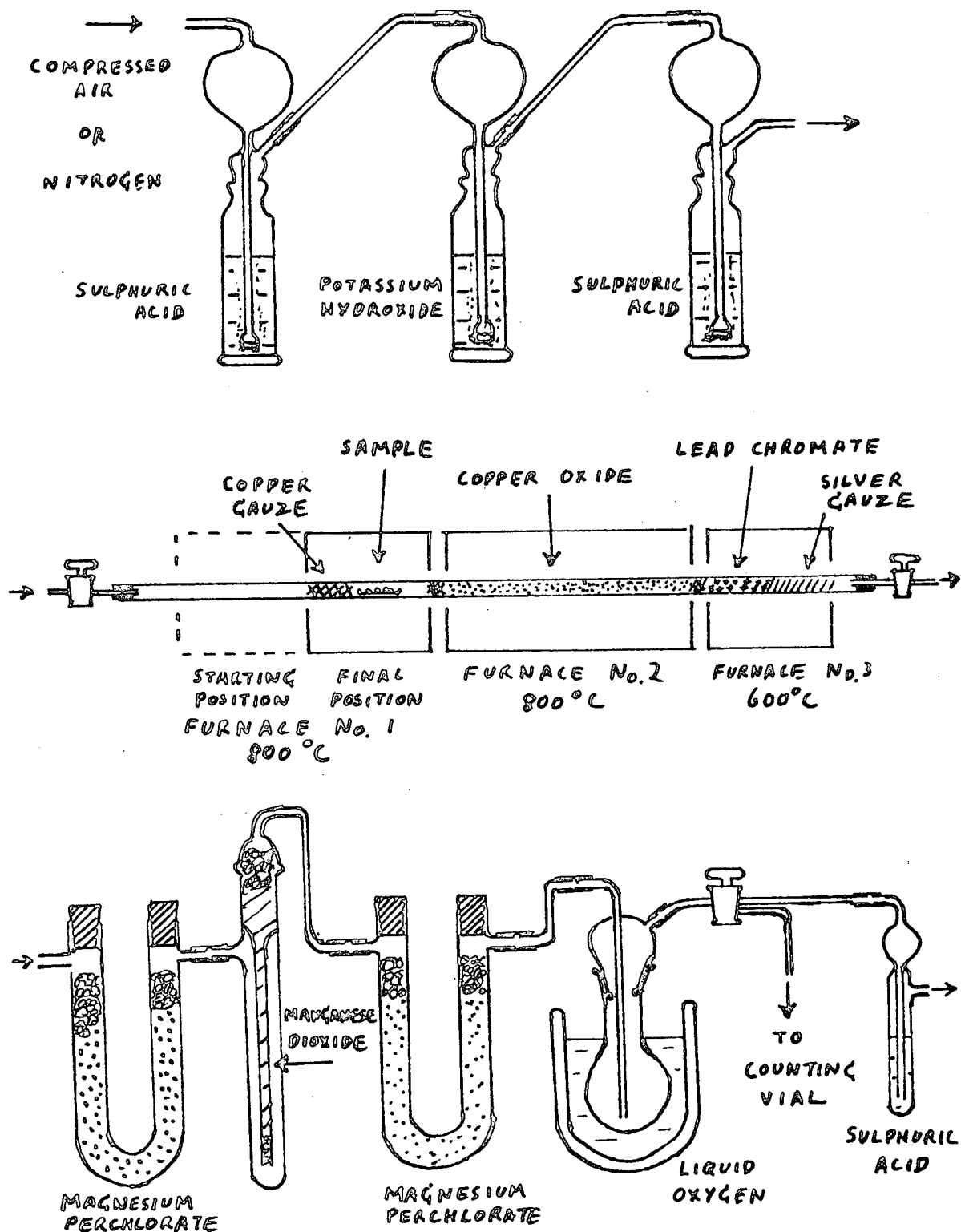
PLATE 5

FURNACES FOR COMBUSTION AND CARBON DIOXIDE EXTRACTION
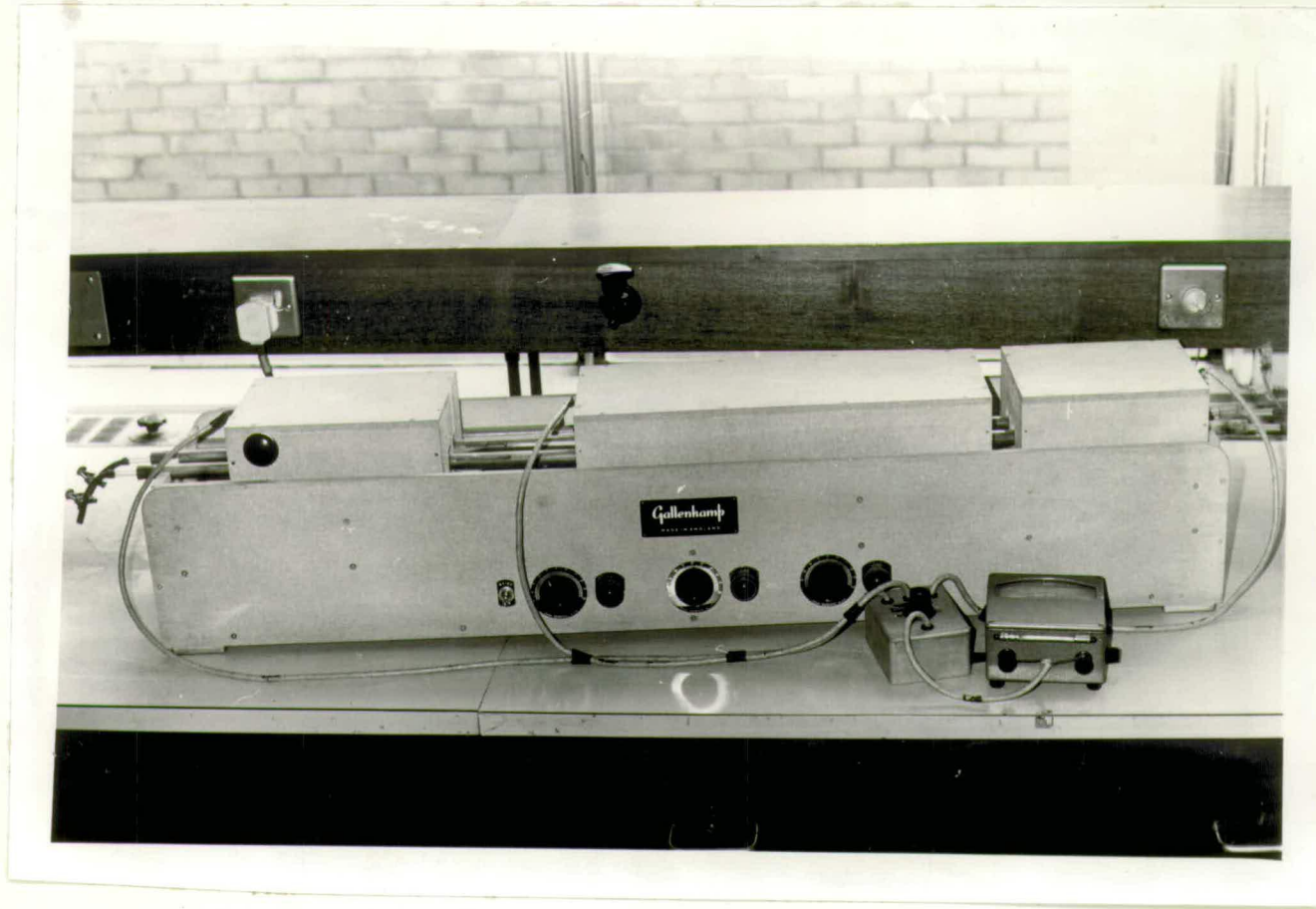
evolved could be calculated from the weight of the original sample provided its carbon content was known. This could be determined by a previous analysis of a similar sample using the same apparatus.

During the combustion process the sample vial was filled with the requisite amount of scintillator (4 gl^{-1} PPO + 0.5 gl^{-1} POPOP in Toluene) and then bubbled with nitrogen to displace dissolved oxygen which would cause quenching.

The vial was then flushed with nitrogen and connected to the flask containing the solid carbon dioxide. The system was evacuated and the carbon dioxide transferred to the vial by removing the liquid oxygen cold trap from the carbon dioxide flask and placing it around the vial. When the transfer was complete nitrogen gas at atmospheric pressure was introduced to the vial which was then stoppered. This last operation was carried out in a glove box which had previously been flushed with nitrogen.

Finally the sealed vial was put in a polythene bag with a drying agent and placed in a refrigerator at $-20^{o}C$ where it was left overnight before counting.

As there was no source of liquid oxygen immediately available a liquid oxygen generator was constructed. This consisted simply of a spiral coil of copper tube immersed in liquid air. Oxygen gas from a cylinder was passed into this and liquified. It was found possible to produce enough liquid oxygen for the cold trap within 30 to 40 minutes. This could conveniently be done during the preliminary heating of the furnaces.

4.6 Calibration and Quenching Correction

Variations in the degree of quenching present from sample to sample will arise mainly from variations in the amounts of carbon dioxide absorbed, and in the optical coupling between vial and photomultipliers. It is essential that this be assessed and suitable adjustments made. It is proposed that assessment of the quenching be done using the channel ratio method with an external source. A suitable source is $^{137}C_s$ emitting γ-rays of energy 660 kev. The spectrum from this source in the radiocarbon energy range (below 156 kev) varies rapidly (Compton edge) and the ratio of two channels in this region should vary strongly with quenching. The quenching correction will then be made by varying the high voltage supplies to the photomultipliers while keeping the counting window fixed.

A preliminary experiment is required to determine the relation between the degree of quenching (channel ratio) and the photomultiplier high voltage. Once this calibration curve is in existence a given sample is assayed as follows:

(a) Determine channel ratio with the external source in position. Since the external source will be reasonably strong this count can be kept short.

(b) The high voltage is selected from the calibration curve and the apparatus adjusted.

(c) The main count is then taken.

When a background count is required a similar procedure is followed.

The preliminary calibration is performed by examining a series of samples containing known amounts of radiocarbon, with varying amounts of a quenching agent, at various values of photomultiplier high voltage. The multichannel analyser is used to determine the spectrum in each case and the counting window appropriate is chosen to give the most significant result using the computer program GATEFIX described in Chapter 5. For each mix the channel ratio with the external standard is determined for a fixed voltage and pair of channels. By graphing the results it is then possible to pick out, for a fixed counting window, the appropriate high voltage to be used for a particular value of the channel ratio.

Although a large number of points are required to obtain the calibration this need be repeated at infrequent intervals only. The activities used should be sufficiently great to allow short count times and use of the computer program keeps the manual computation to a minimum.

CHAPTER 5

Development and Testing of the Radiocarbon Installation

5.1 Computer Program GATEFIX

The object of the program GATEFIX is to select, for the given spectrum of source plus background and the spectrum of background alone, the discriminator gate which will lead to the most significant result. This process has to be performed a number of times during the quenching calibration and the advantage of a rapid means of computation is obvious.

The program which is reproduced in appendix 1 is written in the language Fortran IV and is designed for use on the ICL 1900 Computer of the Mathematics Department at Paisley College of Technology.

The required input data are the experimentally determined points for the two spectra, source plus background, and background alone, and the limits of the discriminator voltage between which the computation is to be performed. Curves are fitted to the spectral points by the least squares method (Subroutine LSTSQUARE). A ninth power curve is used and tests have shown that this gives a good fit for any shape of spectrum which might reasonably be expected.

The coefficients of the spectral curves determined by LSTSQUARE are passed on to subroutine SELECT where they are used to evaluate the relative standard deviation of the count due to the source activity alone, for a range of gate settings between the specific limits. A search for the minimum relative standard deviation then gives the optimum gate setting desired.

A test of the significance of the result is obtained using the relative standard deviation corresponding to the optimum gate and the scientific subroutine F4ERFN which is available as part of the computer soft ware. In addition various tests are incorporated to detect and draw attention to defects in the input data.

The print-out consists of

(1)   the original spectral input data

(2)   the spectrum of the source alone as computed by the least squares fit

(3)   the lower and upper limits of the optimum gate

(4)   the level of significance (percent) of the result.

In the event of it not being possible to complete the computation various comments are available to describe any defects in the input data.

The program was tested using the points plotted in figure 16 and the gate limits shown in the figure were obtained.

5.2   Carbon Extraction System

As described in section 4.5 the carbon extraction system approximates closely to the British Standard. As a similar apparatus had been in routine use in the fuels section of the Chemistry department over a long period and which gave consistently yields of around 100% it was not anticipated that there would be any major difficulty with this part of the installation. Accordingly trial runs were limited to a few only to gain experience in handling the equipment.

FIGURE 16

FICTITIOUS SPECTRA USED TO TEST PROGRAM GATEFIX
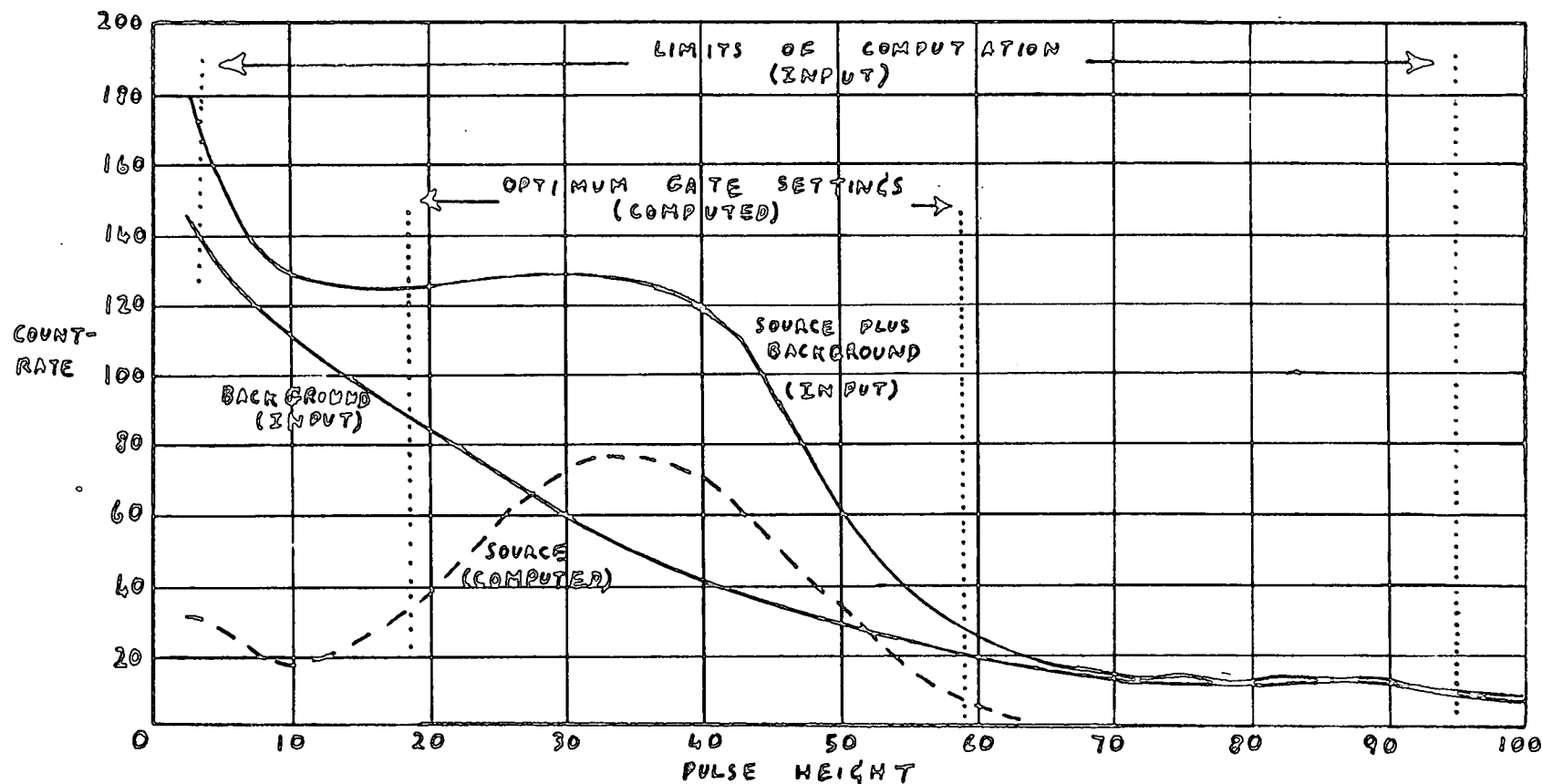
The initial runs surprisingly gave yields in excess of 100%.
This proved to be due to charring of the rubber stoppers at the ends
of the combustion tube and was cured by a slight repositioning of the
furnaces.

Figures of 91% and 91.9% were then obtained in successive runs
using first a standard soda-asbestos absorption tube and then a liquid
oxygen cold trap. An absorption tube placed after the cold trap
recorded only 0.6% of the carbon showing that the cold trap was
efficient. The source of carbon used in all these tests was benzoic
acid which contains 69% carbon by weight and the yields were determined
by weighing.

The low yields obtained latterly were not thought to be serious
as some difficulty had been experienced in maintaining a uniform gas
flow and some leaks were still present in the system. It was expected
that both of these troubles would be eliminated by an alteration to the
gas flow system and by a careful rebuilding of part of the absorption
train and accordingly attention was turned to other parts of the
installation.

An attempt was made at an early stage to use a liquid air cold trap
for the carbon dioxide. However, this also trapped oxygen in the gas
flow and hence it was necessary to go over to a liquid oxygen trap.

5.3 Scintillation Vials

The development work on the vials was mainly concerned with gaining
expertise in handling, and in perfecting and testing the spring
retainers for the stoppers. Since the vials were specially made in

quartz and were quite expensive there could be no question of changing
their design unless it were proved absolutely essential.

The retaining springs had to be selected so that no leakage of
the scintillation fluid would occur for the normal working range of
pressures, but would take place if the pressure rose above this level,
and certainly before the maximum design pressure of the vials was reached.

No springs of exactly the right dimensions and strength were
available. However, it proved easy to shorten the standard retaining
springs sold for this purpose which were themselves too long. The
shortened springs were tested by suspending weights from them and noting
the extension produced. From the resultant curves of tension against
length matched pairs of springs could be picked out which would release
within the desired range of pressures.

After some practice it was found possible to produce shortened
springs with a reasonably consistent performance. Table 4 shows results
obtained with a group of 7 springs showing that 5 out of the 7 were
suitable for use.

Table 4

Spring	A	B	C	D	E	F	G
Critical Tension (gm)	600 ± 50	580	470	700	540	640	600
Crit. Pressure (atmos)	16.4 ± 1.4	15.8	12.8	19.1	14.7	17.5	16.4
Remarks			Reject	Reject			

Curves of tension against length for some of these springs are shown in figure 17.

All of this work was done at room temperature but the correction to working temperature at $-20^{\circ}C$ is of the order of 1% and small compared to both the experimental error and the margin of safety.

Various problems in handling the vials became apparent with experience.

Filling and emptying proved difficult due to the small diameter of the neck. A large size syringe was found convenient to introduce the scintillator fluid. Bubbling with inert gas to displace the dissolved oxygen was done using a micropipette which was also used to introduce air in order to empty the vial after a count.

At liquid air temperatures handling of the vial was done using corrugated rubber gloves such as are sold for domestic purposes. At these temperatures the quartz appeared to become brittle and at an early stage the lugs on the vial to which the stopper retaining springs were attached broke off. To replace them the perspex collars shown in figure 18 were designed and constructed. Since the coefficient of expansion of perspex is greater than that of quartz the collars had to be a slack fit only at room temperature to allow for the difference in contraction to liquid oxygen temperature. These collars proved very successful both as a means of anchoring the springs and by providing supports to hold the vial upright.

FIGURE 17

PERFORMANCE OF A GROUP OF RETAINING SPRINGS
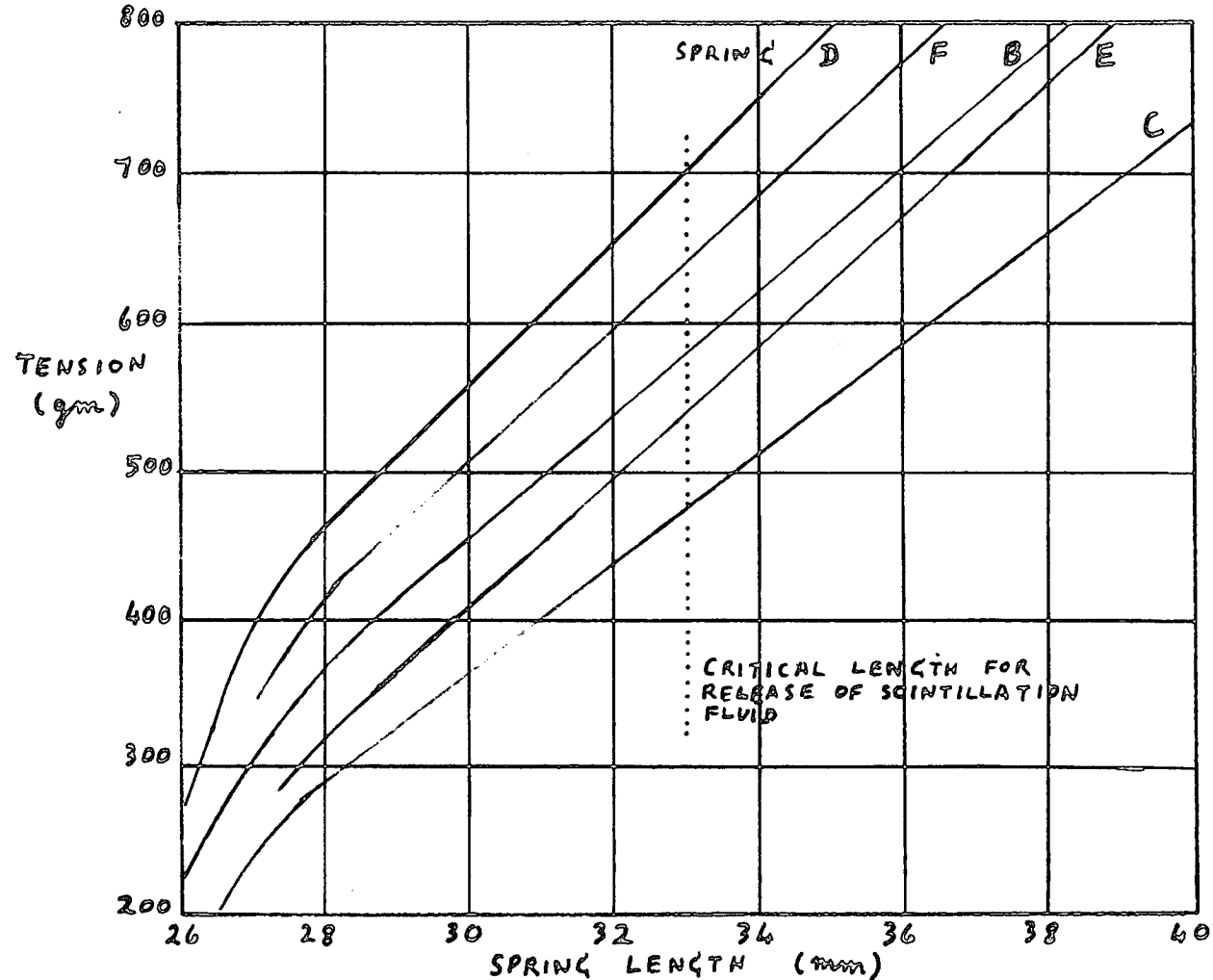
FIGURE 18
RETAINING SPRING COLLARS
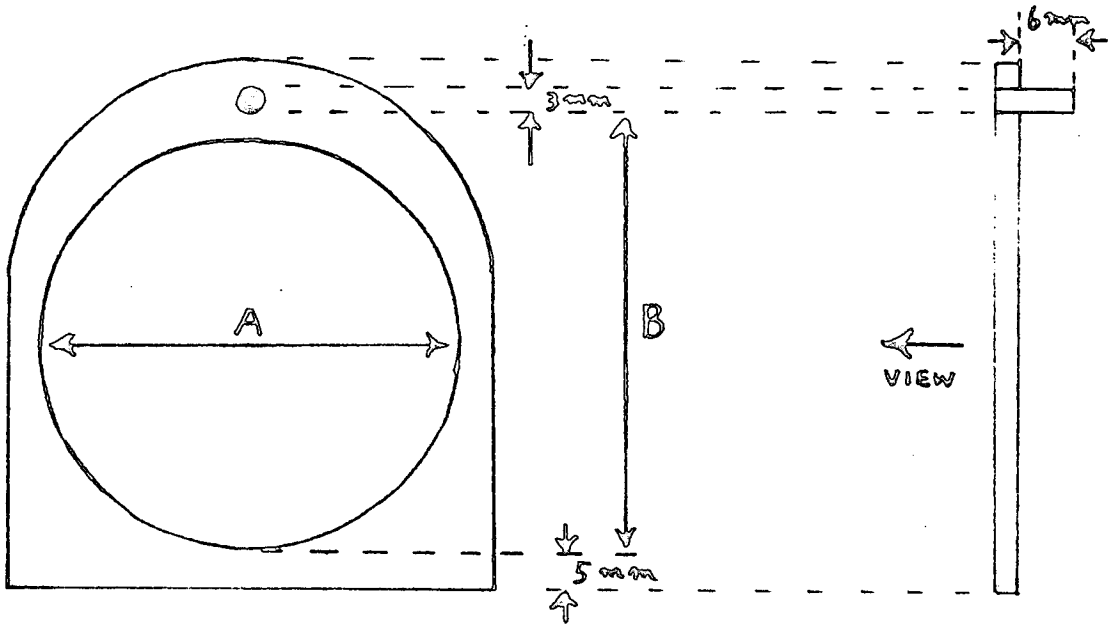
	LARGE VIAL	SMALL VIAL
A	63·8 mm	46·6 mm
B	65·7 mm	48·4 mm

MATERIAL — PERSPEX
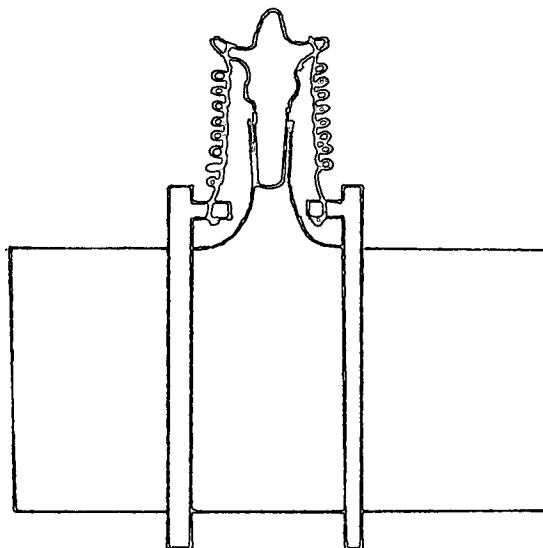
Testing of the vials for strength was performed simply by filling and allowing to heat up to $0^{o}C$. Since only one of each size of vial was in existence it was not possible to test to destruction. At $0^{o}C$ the stopper held firm and there was no leakage of scintillator. For safety a welders protective face mask was worn whenever the vial was handled when under pressure.

Finally some difficulty was experienced in ensuring good optical coupling between vial and photomultipliers. A high viscosity silicon oil (100,000 cs) which had a syrupy consistency was procured and used in place of the oil (20 cs) normally used for this purpose. In the confined space of the counting cell this viscous oil was easy to apply and appeared to give satisfactory coupling.

5.4 Cooling System

The cooling system used cold air boiled off from the liquid phase by means of a heating coil. Tests were required to check its capacity to achieve the desired temperature ($-20^{o}C$), stability and the consumption of liquid air.

Temperatures in the cell were measured by three chromal-alumal thermocouples.

Thermocouple outputs were measured directly using a Scalamp galvanometer and a calibration was obtained by immersing one junction in melting ice and the other in hot water. Additionally a check on the cell temperature was provided by use of the temperature scale on the variable thermostat. A typical calibration curve is shown in figure 19.

FIGURE 19

THERMOCOUPLE CALIBRATION CURVE
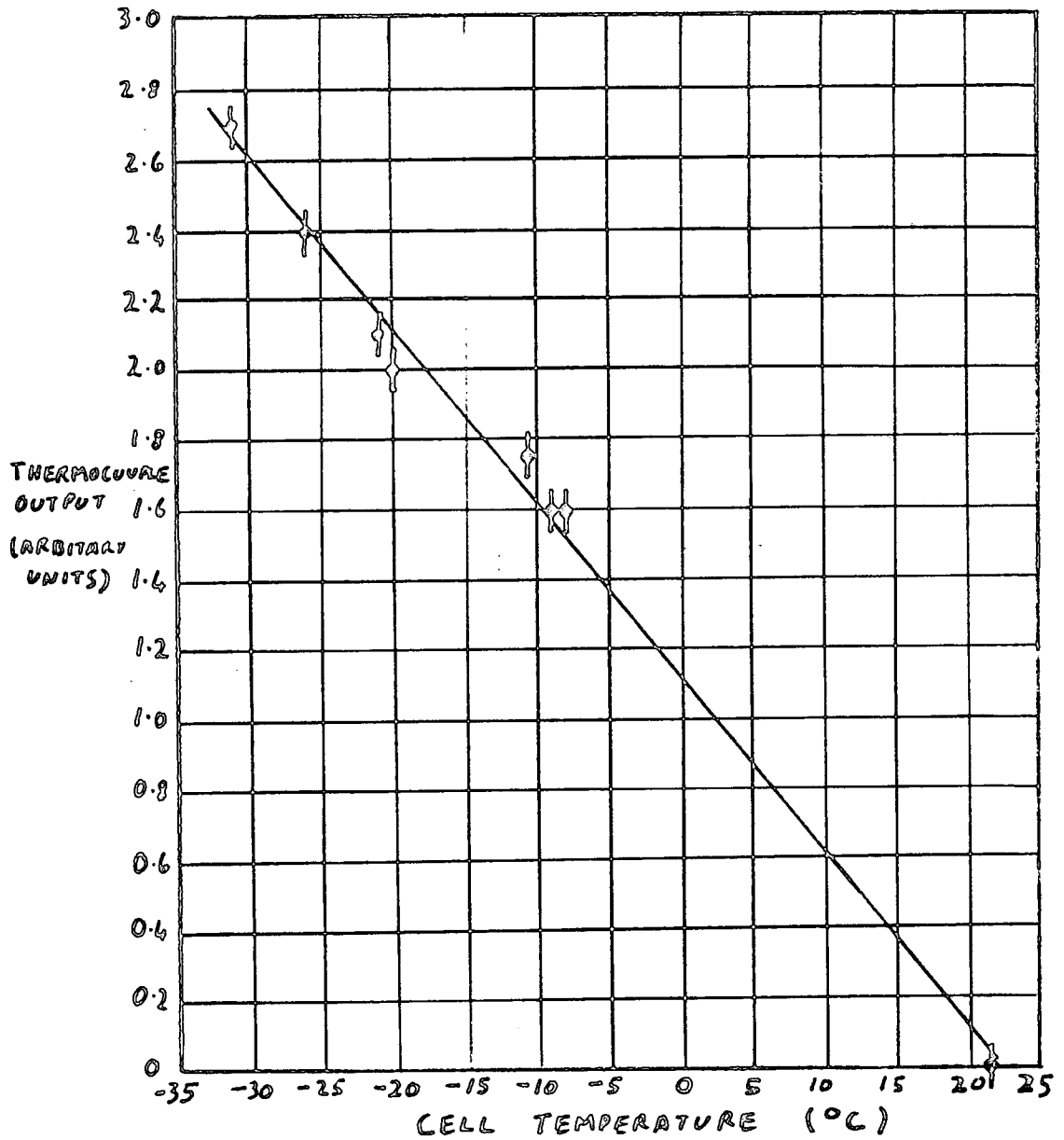
An initial run showed that the three thermocouples gave substantially similar temperatures indicating that the ambient temperature in the cell was uniform in the central region containing the vial. After this one thermocouple only, situated just above the vial, was used.

An extended cooling test lasting for 5 hours produced the curve shown in figure 20. It can be seen that a temperature of $-20^{\circ}C$ is easily attainable and that this is reached some 60 minutes after switching on the system. With increased power $-30^{\circ}C$ is attainable. For normal use a heater power of 166 W (2.5 A) was suitable. The consumption of liquid air during this 5 hour period was 18.3 ℓ or 3.7 litres per hour. A 100 litre dewar might therefore be expected to last for almost a 24 hour run.

On completion of the test the inside of the cell was examined for any trace of moisture which might affect the electronics but none was observed. Cold air evolved in this way is, of course, completely dry and as the cell is operated under slightly positive pressure no moisture from the atmosphere should be able to penetrate.

5.5 Electronics

Although many of the circuits used were based on those described by Kootsey[138] and Elad and Rozen[139] the general arrangement and much of the detail had to be designed specifically for the present application. A considerable amount of test and development work had to be undertaken and this was undoubtedly the most time consuming part of the whole project.

FIGURE 20

COOLING SYSTEM TEST

85.
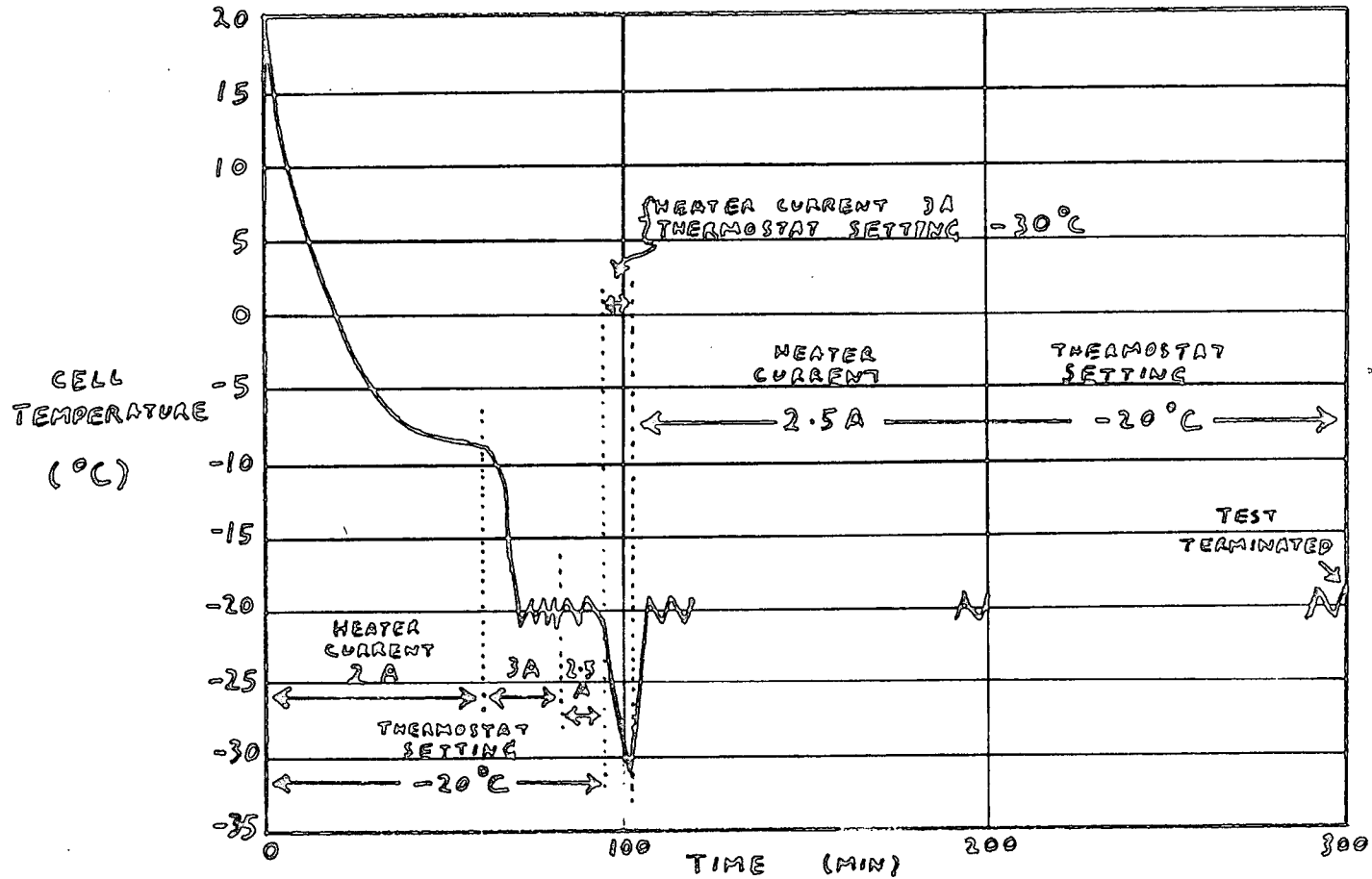
The dynode chain and preamplifier assemblies were standard and performed predictably. Single electron pulses due to dark current were examined using a cathode ray oscilloscope with the photomultiplier in a light tight box. The most notable feature was that these were relatively slow and wide. The rise time was around 2 µs and the width about 10 µs.

From the preamplifier onwards the circuits were constructed in the workshop and each circuit had to be tested individually and collectively. Most trouble was experienced when the circuits were tested collectively and was due to cross pick-up between circuits due to both electro-magnetic signals, and spikes transmitted along the low voltage power lines. Extensive screening and smoothing was introduced and attention paid to lay out.

At this stage it was realised that much of this striving after perfection was unnecessary as the signal pulses were in fact fairly slow and the spurious pulses picked up were fast. In most cases the unwanted pick up could be avoided by adjustment of time constants to render the circuits insensitive to fast pulses. Screening had, however, to be retained for the timing circuits used to operate the gates.

Tests on the electronics separately from the preamplifier photo-multiplier assemblies were of limited value due to the difficulty of exactly simulating the true shape of the input pulses. However, one such set of results aimed at investigating the splitting of the input pulse between the two counting channels is of interest and is shown in figure 21. This shows that the variation of output pulse height with the splitting ratio is small. Since a wide counting window will be used

FIGURE 21

EFFECT OF INPUT SPLITTING RATIO ON OUTPUT

TEST ON ELECTRONICS NOT INCLUDING PRE-AMPLIFIERS

INPUT PULSES TAKEN FROM A PULSE GENERATOR
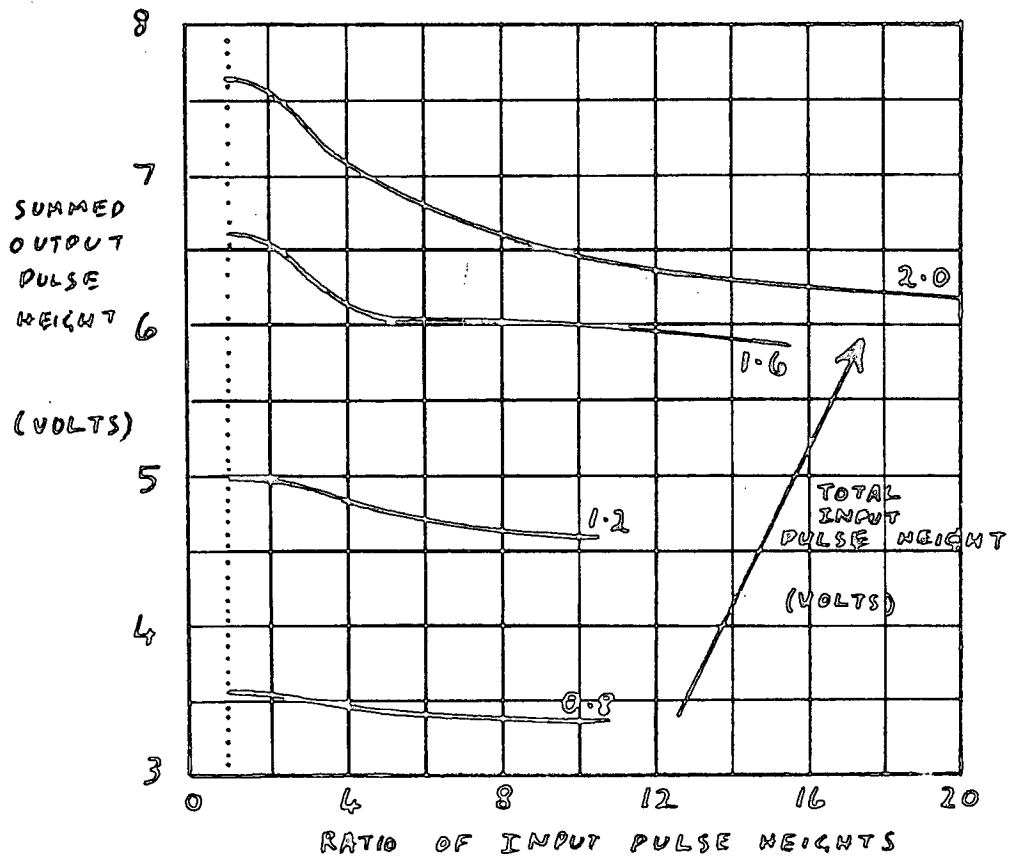
the fall in counting efficiency due to this factor should also be small.

The crucial tests of the electronics occur in situ with the correct operating conditions and these are described in the next section.

5.6   Complete System Tests

A comprehensive series of tests on the complete system was commenced in Autumn 1969.

The first run was intended to investigate separately the characteristics of the three channels using single electron pulses only.   It immediately became obvious that light was penetrating the counting cell despite the interlocking bricks and the internal thermal insulation.   The whole cell was sheathed externally with black polythene sheeting and the experiment continued.   Results for the shield channel are shown in figure 22.   Attempts to repeat these results for the other two channels failed due to discontinuities in interconnecting cables and it was decided to terminate this run at this point and remake all cables.

Tests were resumed using the ratemeter pen recorder spectrometer to monitor the output.   In addition it had now been decided to use three separate high voltage sets to avoid any possibility of cross talk between the channels.   These tests showed that the shield channel and one of the counting channels were working correctly.   The other count channel gave no output and a check on the preamplifier showed that a transistor failure had occurred.

FIGURE 22

SHIELD CHANNEL CHARACTERISTICS

NO SCINTILLATION VIAL PRESENT
COUNTS ORIGINATE FROM PHOTO-MULTIPLIER
PHOTO-CATHODES
COUNT-RATES FOR SECOND CURVE ARE ENHANCED
BY A C_s^{137} γ-SOURCE WITHIN THE CELL
ROOM TEMPERATURE

INTEGRAL COUNT RATE AGAINST P-M. HIGH VOLTAGE
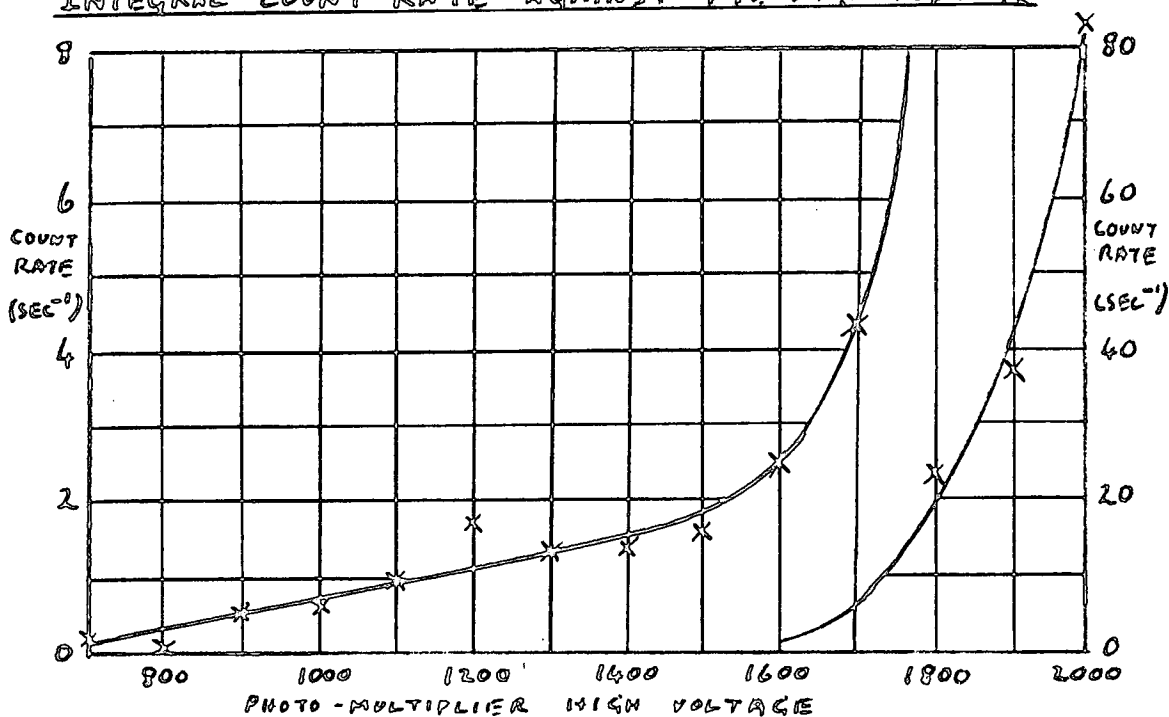
DIFFERENTIAL COUNT-RATE AGAINST DISCRIMINATOR LEVEL
GATE WIDTH = 0.5V   HIGH VOLTAGE = 1200V
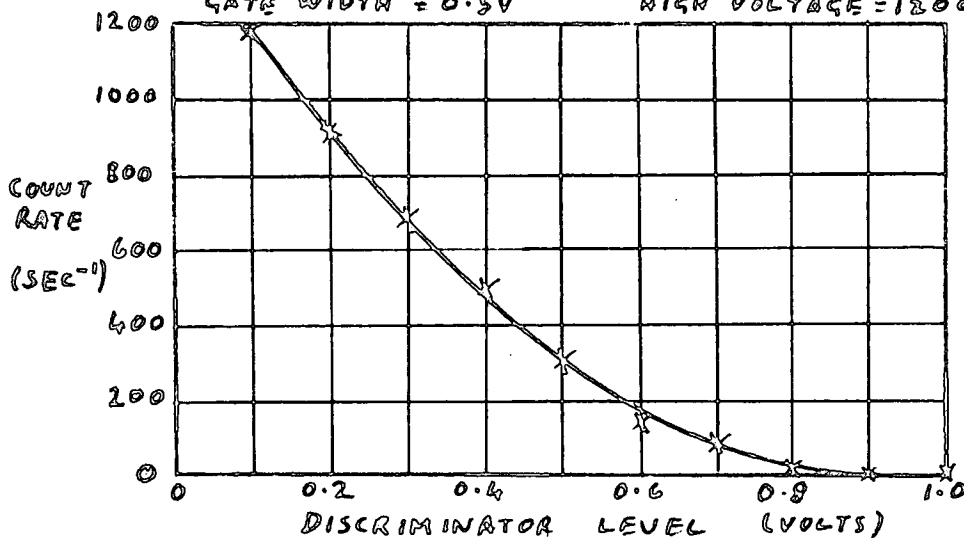
After repair of the preamplifier both count channel preamplifiers were re-tested (table 5) and the system tests resumed. Representations of the pen-recorder outputs are shown in figure 23 and show that all three channels were now operating correctly.

Table 5

Tests on Count Channel Preamplifiers

Channel							
1	Input Pulse Height (Volts)	0.04	0.084	0.19	0.36	4.85	
	Output Pulse Height (Volts)	0.025	0.05	0.14	0.25	3.00	
	Gain	0.6	0.6	0.7	0.7	0.6	
2	Input Pulse Height	0.03	0.06	0.20	0.36	4.5	5.2
	Output Pulse Height	0.02	0.035	0.14	0.25	3.2	3.6*
	Gain	0.7	0.6	0.7	0.7	0.7	0.7

Pulse heights were measured on an oscilloscope and are approximate only.

* Distortion of the output pulse occurred at this point.

Finally the output was taken through the pulse height analyser to the scaler in an attempt to assess the background count in each channel taken separately. The pulse height analyser was used in its integral mode and the discriminator set rather arbitrarily so as to cut out the low energy noise. A 15 minute count in count channel 2 gave a background count-rate of 27.8 pulses min^{-1}.

FIGURE 23

BACKGROUND SPECTRUM IN EACH CHANNEL

REPRESENTATION OF RESULTS OBTAINED WITH PEN RECORDER
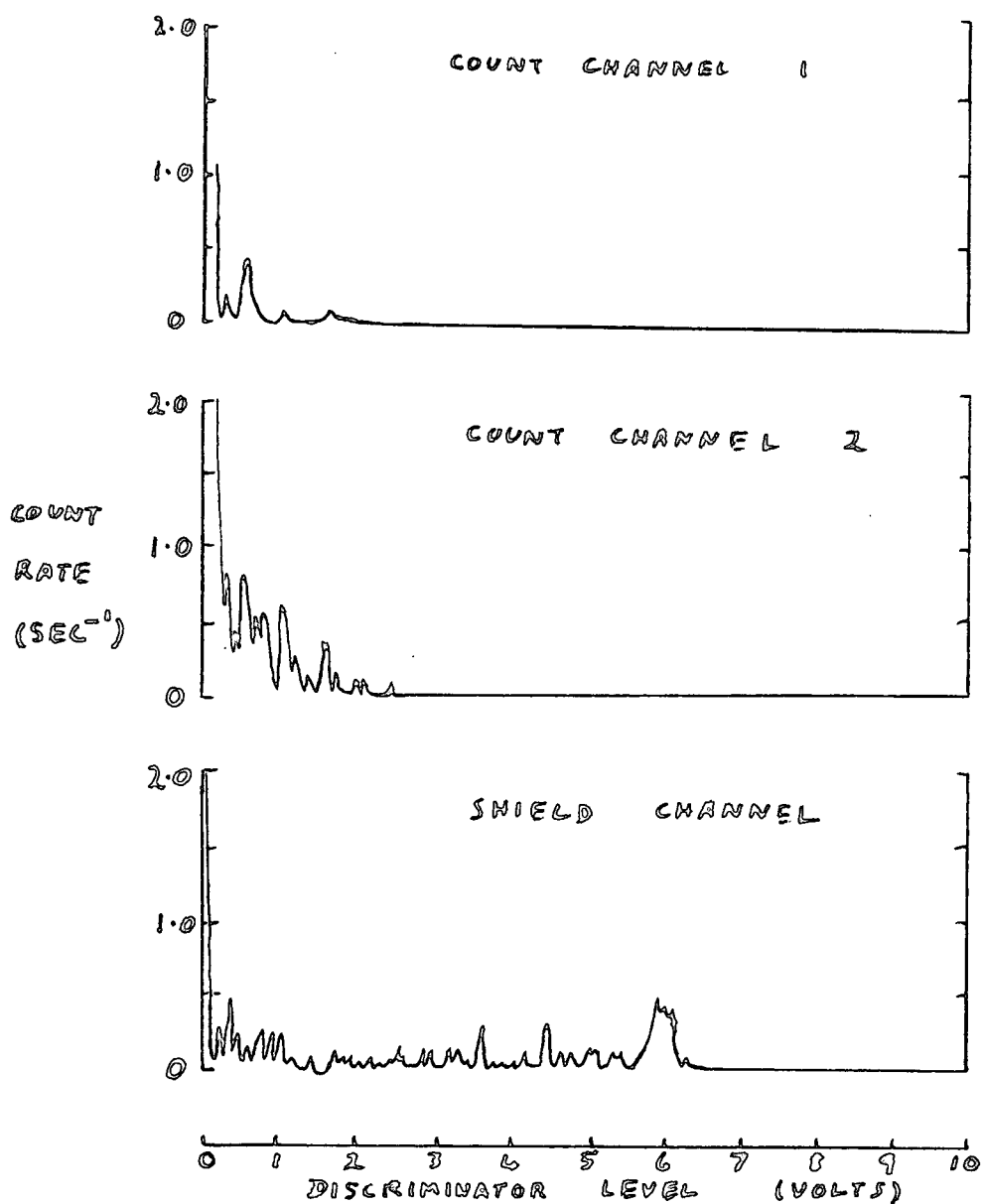
A similar count was commenced in the other count channel but midway through this the scintillator fluid ignited and the run was terminated. The fire was contained within the lead shielding and was extinguished using a carbon dioxide fire extinguisher.

5.7 Aftermath of the Fire

By good fortune the scintillation vial had contained scintillation fluid only at the time of the fire and consequently there was no radioactive contamination problem. Examination of the inside of the cell was possible as soon as it had cooled. This confirmed that the vial had been at the centre of the conflagration as would be expected.

The vial itself was unharmed and the toluene based scintillator had been released via the vial mouth. Whether this was due to a failure of the retaining springs or simply by a pressure release due to a rise in temperature in the vial it was not possible to say. Once the toluene was released it seemed most likely that ignition occurred at one of the photomultiplier pins which were the only exposed points in the circuit. However, there was no evidence to confirm or deny this. The flash point of toluene is low, and ignition would occur readily.

An alternative possibility was that the failure of the cooling system which was the probable cause of the toluene release may have gone so far as to introduce hot air into the system and so also have been the cause of ignition.

The only damage external to the cell was to the cooling system. The heating coil had shorted and the coil former had completely disappeared. Overheating had occurred in the transformer supplying the heater. The level of the liquid air in the dewar was measured just after the fire and was found to be just sufficient to submerge the coil.

The coil former itself had been renewed just previously to this last run and the material used was tuffnol replacing the perspex used previously. The possibility of a reaction involving the tuffnol was suspected and a test was carried out with a piece of tuffnol and the liquid remaining in the dewar. The results were inconclusive, showing that there was indeed a reaction but that it was very mild. It was, however, observed that the fluid remaining in the dewar had taken on the familiar bluish tinge of liquid oxygen. Thus during the five hour run nitrogen (B.P. 77°K) must have been evolved initially whereas towards the end the cooling gas must have been enriched in oxygen (B.P. 90°K) and this would make ignition by whatever means so much easier.

One other possible cause of ignition which was suggested was the failure of the glass envelope of a photomultiplier. One of the photomultipliers had indeed imploded but the chance of this happening spontaneously in coincidence with a release of toluene was too remote for further consideration.

When the equipment is rebuilt in the future it is intended to modify the cooling system so as to avoid the introduction of oxygen to the cell. A possibility is to use liquid nitrogen in place of the liquid air, should this become available. Alternatively gaseous

nitrogen, dried and cooled in a cooling coil immersed in liquid air

might be used. In addition it is considered essential that should

the liquid nitrogen method be possible then the level of the liquid

be continuously monitored and a warning given when this falls to a

dangerous level. A continuous record of the cell temperature using

a pen recorder would also be invaluable both in preventing mishaps

and in subsequently investigating them.

5.8   Conclusions

Despite the premature termination of the experiments the results

obtained show that this is a feasible method for radiocarbon dating.

It is not possible to say whether the target of 50,000 years could

be reached but the one background count of 27.8 pulses min^{-1} obtained

in one channel without the benefits of coincidence noise reduction or

anti-coincidence shielding at least gives cause for hope.

The carbon extraction system has proved relatively easy to use.

The total time required for the extraction of the carbon and its

introduction to the vial is about $2\frac{1}{2}$ hours which would allow 3 vials

to be prepared in a working day ready for counting on the following

day. This compares with a time of 8 hours required for benzene

synthesis in Tamers method. Sample materials are limited to those

which are easy to combust, such as peat and wood and no attempt has

been made to treat difficult materials such as bone.

Modifications are required to the cooling system to avoid any recurrence of a fire hazard. The simplest solution seems to be simply to replace the liquid air used in the past with liquid nitrogen.

Various other modifications are desirable to aid manipulations. In particular a streamlining in the vial filling and emptying procedures would be welcomed. Also the access to the counting cell is by means of a heavy lead plug which must be withdrawn horizontally and this requires considerable physical effort. When rebuilding the system it is intended to arrange for mechanical assistance for this operation.

CHAPTER 6

The Liquid Scintillation Counting of Elemental Carbon in Granular Form

6.1 Introduction

The direct counting of elemental carbon for the purposes of dating has not been examined since the early work of Libby and his associates using the screen wall Geiger counter.

However, the recent development of heterogeneous systems using liquid scintillators opens up new possibilities for the assay of radio-carbon in forms which are insoluble in the scintillator. Most of the work to date on radiocarbon by this method has used barium carbonate as the source material. Barium carbonate contains only 6% carbon by weight but on the other hand will cause much less optical quenching than granular carbon. There does not seem to have been any study of the relative importance of these two factors and of the possibility of achieving greater sensitivities using elemental carbon.

Such heterogeneous systems cannot achieve the performance of the homogeneous methods but might well provide a simple convenient way of dating more recent samples or even simply of deciding on the authen-ticity of alleged aged objects (i.e. whether they are of recent origin or not). The short test program described in this chapter was designed to provide an indication as to the feasibility of dating using granular carbon in a heterogeneous system.

No attention was paid at this stage to the problem of producing the carbon grains as the method used would depend on the grain size distribution found to give the highest counting efficiency. Typical systems are described by Anderson, Arnold and Libby[67] and by Rutherford and Liner[142,143].

6.2 Suspension of Granular Carbon in Toluene

The simplest system is a straight suspension of the source material in the scintillator. Suspensions are subject to variations in counting efficiency with time due to settling, as noted in section 2.5, and this could be a serious problem in dating due to the long count times involved.

Very fine grain carbon is available as colloidal graphite and this would probably give a sufficiently stable suspension. However, it was felt that for a realistic result carbon in a form which it would be reasonably easy to produce in the laboratory as a routine procedure should be used. Accordingly tests were conducted using ordinary laboratory grade charcoal powder ground down manually in an agate mortar and pestle. The representative grain size determined by microscopic observation was 0.5 micron.

A suspension of 0.2 g carbon in 15 ml toluene was prepared and left to stand. Noticeable sedimentation had occurred within 5 minutes and after 30 minutes almost 100% of the carbon had settled.

This rapid settling seemed to rule out the use of carbon suspensions for dating. However, for the sake of comparison and in case finer grained powders were feasible it was thought useful to investigate the light absorbance of a suspension. A suspension was prepared as previously and left to settle for 5 minutes to remove the larger grains. The carbon remaining in suspension was measured by depositing a measured volume of the suspension on filter paper, drying and weighing. A concentration of 0.35 mg carbon per ml was obtained. Samples of this suspension were then tested on a Hilger-Watts grating spectrophotometer

for light in the rays of wavelength from 370 mμ to 650 mμ. The

absorbance relative to pure toluene is plotted in figure 24. Relative

absorbance A is defined in the usual way as

$$A = \log \frac{1}{T} = \log \frac{I_o}{I}$$

where $\quad$ I $\quad$ = $\quad$ intensity of light transmitted by the sample

$\quad\quad$ I_o $\quad$ = $\quad$ intensity of light transmitted by the standard

$\quad\quad$ $T = \dfrac{I}{I_o}$ $\quad$ = $\quad$ transmittance.

6.3 $\quad$ Dispersion of Carbon in a CAB-O-SIL $\quad$- $\quad$ Toluene Gel

Stabilisation of a given suspension can be achieved by the use of

fumed silica to produce a gel. Since the introduction of the silica

will itself reduce the counting efficiency it is important to use just

enough to produce a stable gel.

The proprietary brand of silica known as CAB-O-SIL produced by the

Cabot Corporation in the U.S.A. was used. The CAB-O-SIL was dispersed

in the toluene using a mixer rotated at about 900 rpm for 5 minutes in

all cases.

In order to determine the optimum mix gels were prepared containing

CAB-O-SIL in the range of concentrations 0 to 4% by weight. These were

set aside to settle and it was observed that the solution in each case

separated into a stable gel with a layer of liquid toluene on top.

The percentage by volume of the sample which formed a gel was plotted

against CAB-O-SIL concentration (figure 25) and the concentration to

give 100% gel picked out. This required a slight extrapolation and gave

FIGURE 24

ABSORBANCE SPECTRUM OF CARBON IN TOLUENE SUSPENSION

RELATIVE TO PURE TOLUENE

CARBON CONTENT = 0.35 mg/ml

WAVELENGTH (mμ)
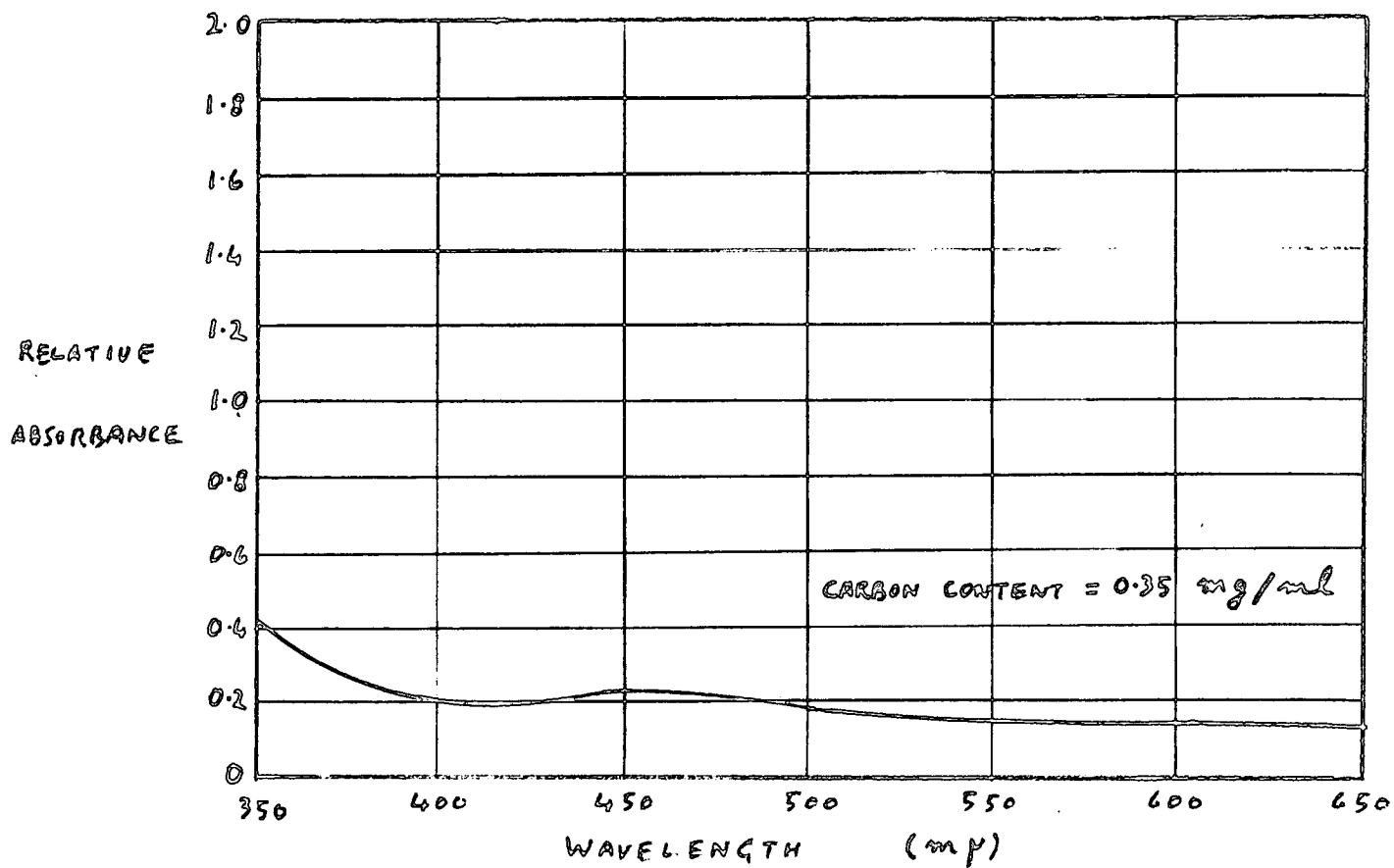
FIGURE 25

VARIATION IN CAB-O-SIL — TOLUENE GELS WITH CAB-O-SIL

CONCENTRATION
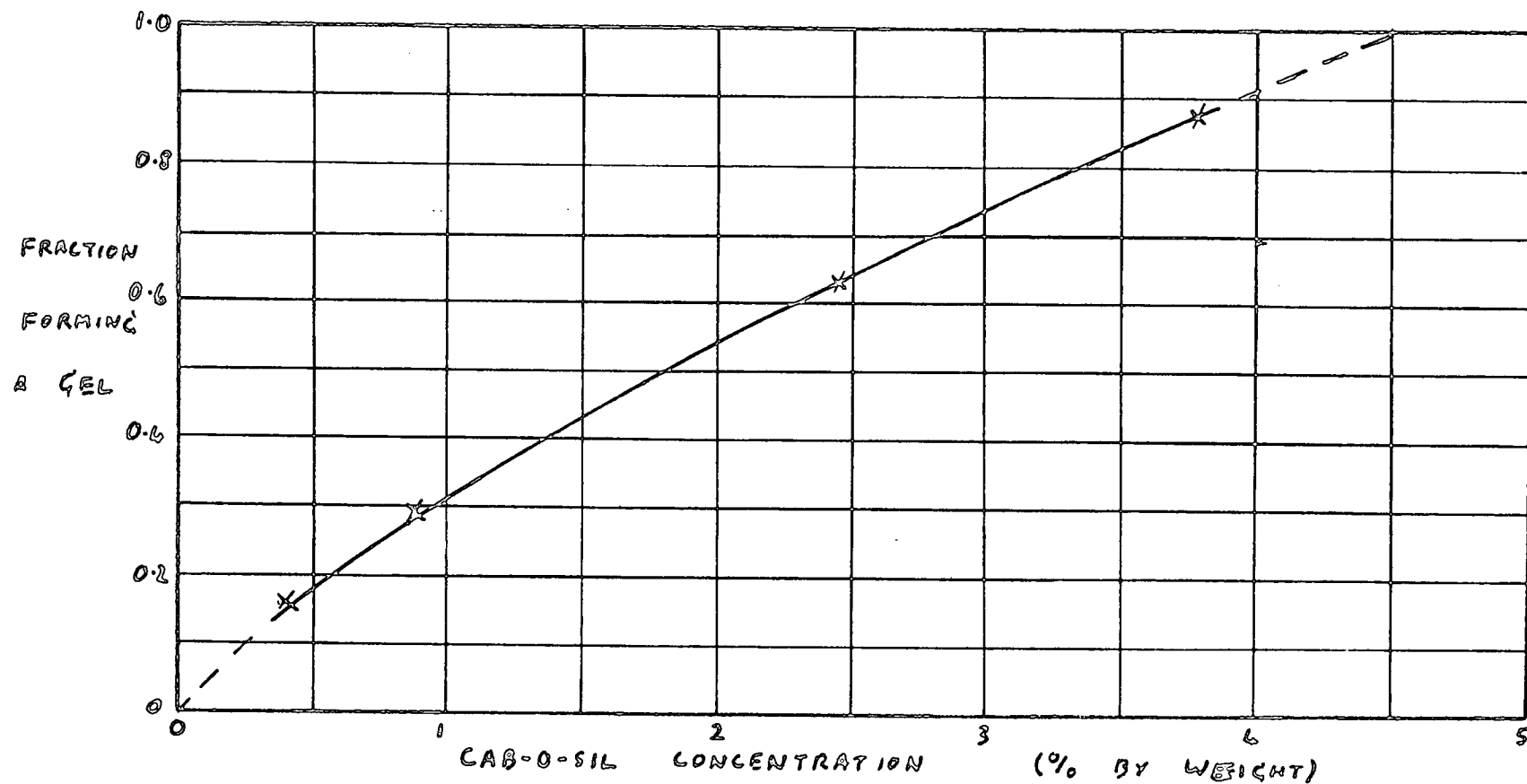
a concentration of 4.5% CAB-O-SIL by weight. This is in general

agreement with the concentrations used by other workers and was used

from this point on.

Gels were then prepared containing various amounts of carbon

and tested on the spectrophotometer. For comparison a gel containing

barium carbonate was also prepared and tested. The $BaCO_3$ powder was

like the carbon, ground down in the agate mortar and pestle. Micro-

scopic examination showed a tendency to form large conglomerates. A

typical grain size was, however, 1 to 2 microns. These results are

shown in figure 26.

As shown by Ross and Yerick[94], it is permissible,for samples with

colour quenching only, to relate the counting efficiency to the relative

absorbance. It was intended to perform a counting experiment with a

standard radiocarbon source to determine counting efficiencies but

there has not as yet been time to do this. However, it is possible to

estimate the performance of the carbon loaded gel by using the results

obtained by Gilly and Bisci[119] for barium carbonate.

If the lowest acceptable counting efficiency is 30% then according

to Gilly and Bisci some 15 mg barium carbonate (0.9 mg carbon) can be

incorporated per ml scintillator.

Assuming then that the relative absorbance of barium carbonate gels

increases linearly with mass of barium carbonate as has been demonstrated

for carbon gels (figure 27) and that the representative wavelength is

400 mμ then the maximum permissible relative absorbance relative to

pure toluene is 0.91. From figure 27 it can be seen that the maximum

amount of granular carbon which it might be possible to incorporate is

approximately 0.5 mg ml^{-1}.

FIGURE 26

ABSORBANCE SPECTRA OF LOADED CAB-O-SIL — TOLUENE GELS

ALL GELS CONTAINED 4.5% CAB-O-SIL BY WEIGHT

ABSORBANCE RELATIVE TO PURE TOLUENE (vertical axis)

CARBON LOADED 1.43 mg CARBON/ml
CARBON LOADED 0.96 mg CARBON/ml
BaCO₃ LOADED 16.4 mg BaCO₃/ml (= 1 mg CARBON/ml)
CARBON LOADED 0.68 mg CARBON/ml
UNLOADED GEL

WAVELENGTH (mμ)
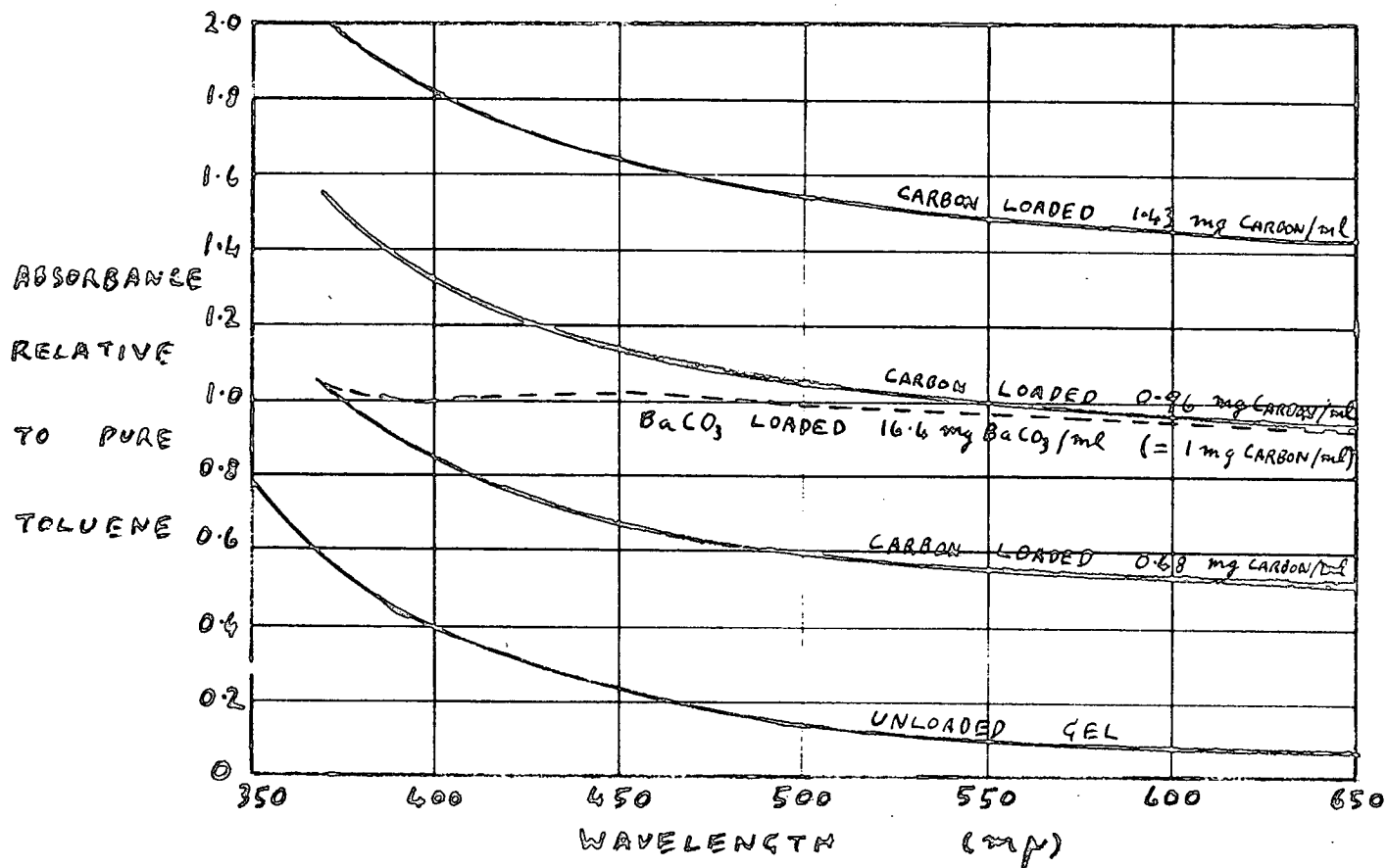
FIGURE 27

VARIATION OF ABSORBANCE OF CARBON LOADED GELS WITH CONCENTRATION OF CARBON AT 400 mµ
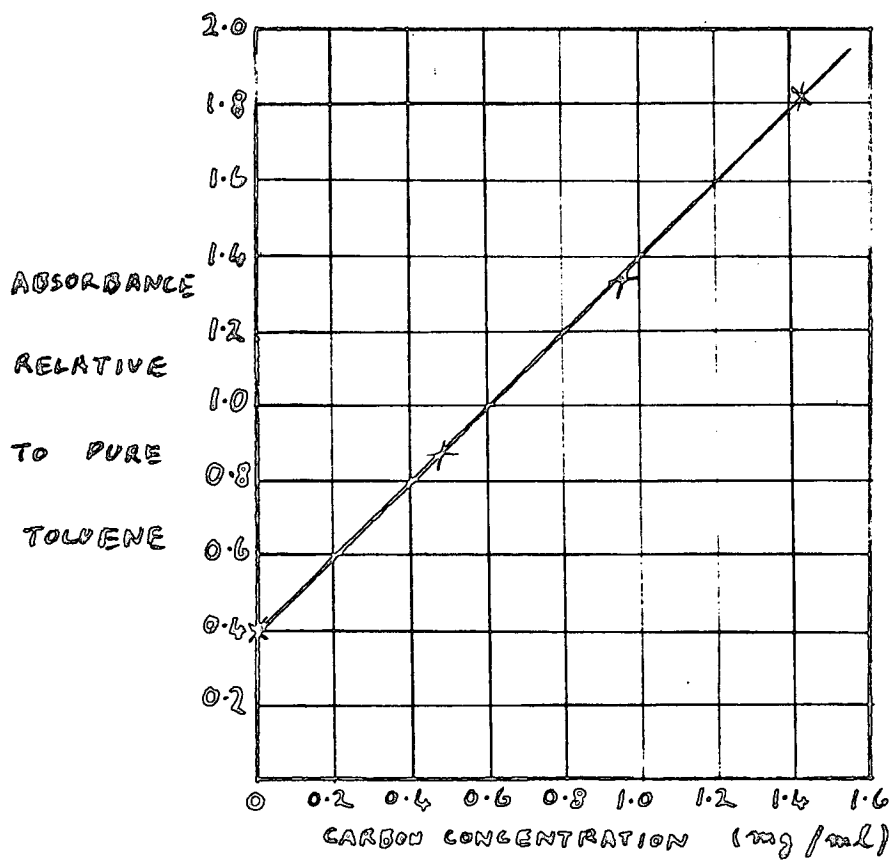
Since the attraction of using elemental carbon is largely due to its simplicity and convenience, feasibility is assessed for a straightforward one channel system with a certain amount of shielding. Gilly and Bisci report a background count rate of 63 min^{-1} using a 60 ml vial and these figures have been assumed here. Use of equations 11 and 12 of Chapter 3 show that it is not possible to achieve reliable dates with this system even with a count time of 48 hours. Authenticity checks are possible for ages greater than 5000 years. However, many of the objects to be examined are likely to be younger than this and the value of the system is limited.

Reduction of the background by improved shielding, coincidence and anti-coincidence circuits, and choice of materials would undoubtedly make dating by this method feasible. However, this elaboration in the counting installation would offset the simplicity and convenience of vial preparation system. Nevertheless, the method might be a useful adjunct to an existing radiocarbon installation with low background equipment already in existence.

6.4 Other Possibilities

Various other possibilities were considered but were not investigated due to lack of time.

A ready mixed gel (NE221) is available from Nuclear Enterprises which merely requires dispersion of the carbon in it before counting. Since CAB-O-SIL is an exceedingly light voluminous material it would be a considerable advantage if the operation of dispensing it could be avoided.

Stabilisation of the carbon suspension by use of an emulsifier such as TRITON X-100 is another possibility. A possible advantage is that the carbon could be in suspension in a second fluid, such as water, which is immiscible with the scintillator.

Another approach might be to search for a simple inorganic material which contains carbon in greater quantity than barium carbonate but which has a similar light absorbance when in suspension. Apart from some work by Harlan[120] on sodium carbonate and bicarbonate a sustained search does not seem to have been made.

Finally it should be remembered that all the tests reported here were carried out with the same type of carbon. It is possible that an examination of the effects of variations in grain size might indicate how a larger amount of carbon might be introduced.

6.5 Conclusions

A radiocarbon dating installation in which elemental carbon in granular form is suspended in a gel, and counted by the liquid scintillation method is feasible only if a good low background counting system is used. The method does not seem worthwhile unless the low background system is already in existence for another purpose.

Barium carbonate loaded gels give somewhat better performance than the carbon equivalent. A material which is as simply prepared from carbon dioxide as is barium carbonate, which has the same optical properties on suspension as barium carbonate, but which contains a higher proportion of carbon would make for an attractive system. It is concluded that this is probably the most fruitful avenue for investigation in this field.

APPENDIX I

Computer Program GATEFIX

(See Section 5.1)

```
    SHORTLIST(LP)
    SEND TO (ED,ICLA-DEFAULT.PFZ9)
    LIBRARY (ED,SUBGROUPFSCE)
    LIBRARY (ED,SUBGROUPSRF7)
    PROGRAM (PFZ9 GATE FIX)
C      SELECTS BEST GATE FOR USE IN COUNTING EXPERIMENT TO DISTINGUISH
C      SOURCE FROM BACKGROUND      (MAX NO OF SPECTRAL POINTS IS 100)
C      DATA INTEGER NO OF POINT IN SPECTRUM OF SOURCE PLUS BACKGROUND
C            REAL SET OF COUNTS FOLLOWED BY SET OF DISCRIMINATOR LEVELS
C                 FOR SOURCE PLUS BACKGROUND
C          INTEGER NO OF POINTS IN SPECTRUM OF BACKGROUND ALONE
C          REAL SET OF COUNTS FOLLOWED BY SET OF DISC LEVELS FOR BACKG
C          REAL LOWER FOLLOWED BY UPPER LEVELS BETWEEN WHICH
C                 COMPUTATION IS TO BE MADE
    INPUT 1=TR0
    OUTPUT 2,(MONITOR)=LP0
    TRACE 2
    END


    MASTER GATE FIX
    READ (1,1)N
  1 FORMAT (I10)
    DIMENSION D(100,2)
    READ (1,2)((D(I,J),I=1,N),J=1,2)
  2 FORMAT (200 F0.0)
    INTEGER P
    P=9
    DIMENSION AT(10)
    CALL LSTSQUARE (N,P,D,AT)
    WRITE (2,3)
  3 FORMAT (/23H SOURCE PLUS BACKGROUND/24H      COUNTS    DISCRIMINATOR/
    K=1
  5 DP=D(K,1)
    DR=D(K,2)
    WRITE (2,4)DP,DR
  4 FORMAT(2F10.5)
    K=K+1
    IF (K.LE.N) GOTO 5
    READ (1,1)N
    READ (1,2)((D(I,J),I=1,N),J=1,2)
    DIMENSION AB(10)
    CALL LSTSQUARE (N,P,D,AB)
    WRITE (2,6)
  6 FORMAT (/20H      BACKGROUND ALONE/24H      COUNTS    DISCRIMINATOR/)
    K=1
  7 DP=D(K,1)
    DR=D(K,2)
    WRITE (2,4)DP,DR
    K=K+1
    IF(K.LE.N)GOTO 7
```

```
      DIMENSION AS(10,2)
      DO 8 I=1,10
    8 AS(I,1)=AT(I)
      DO 9 J=1,10
    9 AS(J,2)=AB(J)
      READ (1,10)EL,EM
   10 FORMAT (2 F0.0)
      WRITE (2,20)
   20 FORMAT (/13H SOURCE ALONE/24H    COUNTS   DISCRIMINATOR/)
      DO 21 NS=1,N
      YX=D(NS,2)
      Y=0.0
      DO 22 L=1,10
   22 Y=Y+(AT(L)-AB(L))*(YX**(L-1))
   21 WRITE (2,4)Y,YX
      CALL SELECT (AS,EL,EM,E10,E20,MT,C)
      IF (MT-1)0,13,15
      WRITE (2,12)E10,E20
   12 FORMAT (13H LOW LEVEL    F7.3,16H    HIGH LEVEL    F7.3)
      GOTO 23
   13 WRITE (2,14)
   14 FORMAT (14H ERROR IN DATA)
      GOTO 19
   15 IF (MT.GT.2) GOTO 16
      WRITE (2,11)
   11 FORMAT (46H NO MINIMUM FOUND   LIMITS MAY NEED ADJUSTMENT)
      GOTO 19
   16 WRITE (2,17)
   17 FORMAT (40H DATA DOES NOT GIVE A SIGNIFICANT RESULT)
   23 WRITE (2,18)C
   18 FORMAT (23H LEVEL OF CONFIDENCE    F7.2,10H   PER CENT)
   19 CONTINUE
      STOP
      END

      FUNCTION DET(X,N)
      DOUBLE PRECISION X,Z,B
      DIMENSION X(10,10),Z(10,10),B(10)
      N=N-1
      A=1.0
      A1=1.0
      IF(N-1)102,102,0
      KR=1
      GOTO 133
  107 A=(A*SNGL(X(1,1)))
      KS=2
      GOTO 146
  105 DO 144 K=2,N+1
  144 X(K,1)=(X(K,1))/X(1,1)
      DO112 I=1,N
      DO 112 J=1,N
  112 Z(I,J)=(X(I+1,J+1)-X(I+1,1)*X(1,J+1))
      N=N-1
      IF(N)103,103,0
      GOTO 134
```

```
108 A=(A*SNGL(Z(1,1)))
    KS=1
146 IF(KR.GT.1) GOTO 147
    IF(ABS(A).GT.1.0E50) GOTO 143
    IF(ABS(A).LT.1.0E-50) GOTO 143
    GOTO 147
143 A1=A
    A=1.0
    KR=KR+1
147 IF(KS.GT.1) GOTO 105
110 DO 145 K=2,N+1
145 Z(K,1)=(Z(K,1))/Z(1,1)
    DO 113 I=1,N
    DO 113 J=1,N
113 X(I,J)=(Z(I+1,J+1)-Z(I+1,1)*Z(1,J+1))
    N=N-1
    IF(N)102,102,0
    GOTO 133
101 DO 114 J=1,N+1
114 B(J)=X(1,J)
    DO 115 J=1,N+1
115 X(1,J)=X(K,J)
    DO 116 J=1,N+1
116 X(K,J)=B(J)
    GOTO 132
106 A=(((-1)**(K+L)))*(A*SNGL(X(1,1)))
    KS=2
    GOTO 146
104 DO 120 J=1,N+1
120 B(J)=Z(1,J)
    DO 121 J=1,N+1
121 Z(1,J)=Z(K,J)
    DO 122 J=1,N+1
122 Z(K,J)=B(J)
    GOTO 142
137 A=(((-1)**(K+L)))*(A*SNGL(Z(1,1)))
    KS=1
    GOTO 146
133 IF (ABS(X(1,1)).GE.0.1E-50) GOTO 107
    MP=1
    K=1
    L=1
    I=1
    J=2
123 IF(ABS(X(K,L)).LT.ABS(X(I,J))) GOTO 125
126 IF(J.GT.N) GOTO 124
    J=J+1
    IF(MP-1)123,123,135
124 IF(I.GT.N) GOTO 127
    I=I+1
    J=1
    IF(MP-1)123,123,135
125 K=I
    L=J
    GOTO 126
```

```
127 IF((K+L).EQ.2) GOTO 109
    IF(MP-1)0 ,0,141
    IF(K.EQ.1) GOTO 131
    GOTO 101
132 IF(L.EQ.1) GOTO 106
131 DO 128 J=1,N+1
128 B(J)=X(J,1)
    DO 129 J=1,N+1
129 X(J,1)=X(J,L)
    DO 130 J=1,N+1
130 X(J,L)=B(J)
    GOTO 106
134 IF(ABS(Z(1,1)).GE.0.1E-50) GOTO 108
    MP=2
    K=1
    L=1
    I=1
    J=2
135 IF(ABS(Z(K,L)).LT.ABS(Z(I,J))) GOTO 125
    GOTO 126
141 IF(K.EQ.1) GOTO 136
    GOTO 104
142 IF(L.EQ.1) GOTO 137
136 DO 138 J=1,N+1
138 B(J)=Z(J,1)
    DO 139 J=1,N+1
139 Z(J,1)=Z(J,L)
    DO 140 J=1,N+1
140 Z(J,L)=B(J)
    GOTO 137
109 IF(MP-1) 0 ,0,111
    X(1,1)=0.0
    GOTO 102
111 Z(1,1)=0.0
103 X(1,1)=Z(1,1)
102 DET=SNGL(X(1,1))*A*A1
    RETURN
    END

    SUBROUTINE LSTSQUARE (N,P,D,A)
    INTEGER P,S
    DIMENSION A(10)
    DOUBLE PRECISION BD,X
    DIMENSION B(10,10),Y(10),BD(10,10),D(100,2),DX(100,2),X(10,10)
    K=1
    S=1
    L=1
213 IF(D(S,K).LE.D(S+L,K)) GOTO 212
    L=L+1
    IF((S+L)-N) 213,215,215
212 S=S+L
    IF(S-N) 0,215,215
    L=1
    GOTO 213
```

```
215 IF(K.EQ.1) GOTO 214
    VX=D(S,K)
    DO 217 S=1,N
217 DX(S,K)=(D(S,K))/VX
    GOTO 216
214 VY=D(S,K)
    DO 218 S=1,N
218 DX(S,K)=(D(S,K))/VY
    K=K+1
    S=1
    L=1
    GOTO 213
216    DO 201 I=1,P+1
    Y(I)=0
    K=1
202 Y(I)=((DX(K,2))**(I-1))*DX(K,1)+Y(I)
    K=K+1
    IF (K.LE.N) GOTO 202
201 CONTINUE
    B(1,1)=N
    DO 203 I=2,P+1
    DO 203 J=1,P+1
    B(I,J)=0
    K=1
204 B(I,J)=(DX(K,2))**(I+J-2)+B(I,J)
    K=K+1
    IF (K.LE.N) GOTO 204
203 CONTINUE
    DO 211 J=2,P+1
    B(1,J)=0
    K=1
209 B(1,J)=(DX(K,2))**(J-1)+B(1,J)
    K=K+1
    IF(K.LE.N)GOTO 209
211 CONTINUE
    DO 225 I=1,P+1
    DO 225 J=1,P+1
225 X(I,J)=DBLE(B(I,J))
    DC=DET(X,P+1)
    DO 205 L=1,P+1
    IF(L.EQ.1)GOTO 207
    DO 208 J=1,L-1
    DO 208 M=1,P+1
208 BD(J,M)=DBLE(B(J,M))
207 DO 206 K=1,P+1
206 BD(L,K)=DBLE(Y(K))
    IF(L.GT.P)GOTO 235
    DO 210 J=L+1,P+1
    DO 210 M=1,P+1
210 BD(J,M)=DBLE(B(J,M))
235 DT=DET(BD,P+1)
205 A(L)=(DT)*VY/(DC*(VX**(L-1)))
    RETURN
    END
```

```
      SUBROUTINE SELECT (AS,EL,EM,E10,E20,MT,C)
      DIMENSION AS(10,2),Z(100)
      M=2
314   DO 303 I=1,100
323   E2=(0.01*(I-1)*(EM-EL))+EL
      IF (M-1)325,325,0
      E1=E2
      E2=EM
      IF(E1.GE.E2) GOTO 309
      GOTO 313
325   IF(E1.LT.E2)GOTO 313
      I=I+1
      K=I
      IF(I.LT.100)GOTO 323
      GOTO 310
313 0    XT=AS(1,1)*(E2-E1)+(AS(2,1)*((E2**2)-(E1**2)))/2
    1    +(AS(3,1)*((E2**3)-(E1**3)))/3+(AS(4,1)*((E2**4)-(E1**4)))/4
    2    +(AS(5,1)*((E2**5)-(E1**5)))/5+(AS(6,1)*((E2**6)-(E1**6)))/6
    3    +(AS(7,1)*((E2**7)-(E1**7)))/7+(AS(8,1)*((E2**8)-(E1**8)))/8
    4   +(AS(9,1)*((E2**9)-(E1**9)))/9+(AS(10,1)*((E2**10)-(E1**10)))/1
      IF(XT)315,0,0
    0    XB=AS(1,2)*(E2-E1)+(AS(2,2)*((E2**2)-(E1**2)))/2
    1    +(AS(3,2)*((E2**3)-(E1**3)))/3+(AS(4,2)*((E2**4)-(E1**4)))/4
    2    +(AS(5,2)*((E2**5)-(E1**5)))/5+(AS(6,2)*((E2**6)-(E1**6)))/6
    3    +(AS(7,2)*((E2**7)-(E1**7)))/7+(AS(8,2)*((E2**8)-(E1**8)))/8
    4   +(AS(9,2)*((E2**9)-(E1**9)))/9+(AS(10,2)*((E2**10)-(E1**10)))/1
      IF(XB)315,0,0
303   Z(I)=(SQRT(XT+XB))/(XT-XB)
      NX=1
      GOTO 318
315   IF(I-2)309,309,0
302   J=I-1
      GOTO 316
318   J=100
      IF(M-1)326,326,316
316   K=1
326   LN=1
319   IF(Z(K).LT.0.0)GOTO 306
307   IF(Z(K+LN).LT.0.0)GOTO 321
      IF(Z(K)-Z(K+LN))304,305,306
321   IF(NX.EQ.1)GOTO 305
304   LN=LN+1
      IF((K+LN)-(J+1))0,308,309
      NX=0
      GOTO 307
306   K=K+LN
      LN=1
      IF(K-J)319,310,309
305   LN=LN+1
      IF((K+LN)-(J+1))0,310,309
      NX=1
      GOTO 307
```

```
308  IF(M-1)317,317,0
     E10=0.01*(K)*(EM-EL)+EL
     M=M-1
     K=1
     E1=E10
     GOTO 314
309  MT=1
     GOTO 301
322  MT=3
     GOTO 301
310  MT=2
     GOTO 301
317  E20=0.01*K*(EM-EL)+EL
     X=1/((Z(K))*(1.4142))
     CALL F4ERFN (X,ERF,ERFC)
     C=100.0*ERF
     IF(ERFC.GT.0.3174)GOTO 322
     MT=0
301  RETURN
     END
     FINISH
****
```

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