

GEOLOGICAL  
SURVEY  
OF  
CANADA

DEPARTMENT OF ENERGY,  
MINES AND RESOURCES

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PAPER 66-45

THE GEOLOGICAL SURVEY OF CANADA  
RADIOCARBON DATING LABORATORY

(Report, 7 tables, and 16 figures)

W. Dyck



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OF CANADA

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RADIOCARBON DATING LABORATORY

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DEPARTMENT OF ENERGY, MINES AND RESOURCES

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### ABSTRACT

The Radiocarbon Dating Laboratory of the Geological Survey of Canada began  $C^{14}$  age-determinations in 1961, using a 2-litre copper counter inside a 9-ton background shield consisting of 8-inch iron, 4-inch paraffin, a ring of 23 cosmic-ray guard tubes, and 1 inch of mercury. The background, standard, and meson counting rates at an operating pressure of 150 cm Hg using  $CO_2$  as the counting gas are 1.3 c/m, 20.2 c/m, and 165 c/m, respectively.

In 1964 a 5-litre counter was put into operation. At 4 atmospheres this counter has a background of 3.1 c/m, a modern wood count of 111.0 c/m, and a meson rate of 268 c/m, thus permitting an extension of the age range to 54,000 years from a previous maximum of 40,000 years, using the 4 sigma criterion.

Samples are burned in a stream of oxygen and the  $CO_2$  released is purified on passage through a series of chemicals and traps.

Approximately 450 age determinations of materials of geological interest, most of which have been reported in Radiocarbon, volumes 4, 5, 6, and 7, have been completed during the 5-year period 1961-1965. In addition approximately 50 geochemical samples, including tree rings from a Douglas fir from Vancouver Island and modern maple leaves and grass from Ottawa have been analyzed. Results of investigations of sample contamination indicate that many sea shells are slightly contaminated, resulting in ages that may be in error by several hundred years; no contamination has so far been found in peat samples.



## THE GEOLOGICAL SURVEY OF CANADA RADIOCARBON DATING LABORATORY

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### INTRODUCTION

Radiocarbon is a naturally occurring radioactive isotope of carbon, with an atomic weight of 14, a natural atmospheric abundance of approximately  $10^{-10}$  per cent, and a half life of 5,730 years (Godwin, 1962).

The discoveries that cosmic rays produce neutrons in the upper atmosphere (Rumbaugh and Locher, 1936; Agnew et al., 1947) and that neutrons react with nitrogen atoms to produce a radioactive isotope of carbon (Kamin, 1963) paved the way for the monumental work of Libby (1955), on the radiocarbon dating method.

$C^{14}$  is continuously produced by cosmic ray neutrons in the earth's atmosphere, oxydized to  $CO_2$  by atmospheric oxygen, and in this form takes part in the life cycle of  $CO_2$ , i.e. plants absorb the  $CO_2$  from the air, animals eat the plants,  $CO_2$  exchange between the atmosphere and the ocean provides a continuous supply of  $C^{14}$  for all marine life, decaying organic matter returns the  $CO_2$  to the atmosphere, and so on, in an endless cycle. Hence all living organisms reflect the  $C^{14}$  concentration of the medium from which they draw their carbon. When an organism dies carbon uptake stops, but the incorporated  $C^{14}$  continues to decay at a fixed rate determined only by its decay constant. The amount of  $C^{14}$  in a specimen can be measured in the laboratory, and by combining this with the  $C^{14}$  concentration in the specimen when it was living together with the decay constant of  $C^{14}$ , the time elapsed since the organism died may be calculated. The live or zero age  $C^{14}$  concentration is determined by measuring the natural  $C^{14}$  concentration of a living organism and assuming that the unknown had the same  $C^{14}$  concentration when it was living.

Hence the radiocarbon dating method is based essentially on the assumption that there has been a constant rate of production and distribution of  $C^{14}$  in the various exchangeable carbon reservoirs of the earth.

Libby (1955) obtained experimental evidence in support of this assumption by comparing the  $C^{14}$  ages of samples with ages determined from historical records and tree-ring counts, and finding them in agreement. Kulp (1954) compared  $C^{14}$  ages with measurements based on the production of ionium and with historical ages and found that agreement between the two was within  $\pm 10$  per cent suggesting that both methods are valid and that  $C^{14}$  production and distribution rate has not varied by more than 20 per cent.

Finally, theoretical arguments favour a more or less constant cosmic ray flux over time intervals comparable to the useful range of the  $C^{14}$  method (i.e. from 200 to 50,000 years), hence a constant rate of production



of  $C^{14}$  on earth. In fact, Heymann and Schaffer (1962) measured the cosmic-ray-produced ratio of  $^{39}\text{Ar}/^{36}\text{Cl}$  in iron meteorites and found it to be about the same as that produced by 6.2 Bev protons in iron, indicating that the cosmic ray intensity in space during the last 300,000 years has not changed noticeably.

However, significant changes in the composition of the earth's atmosphere and/or the earth's magnetic field strength, could result in variations of the  $C^{14}$  production rate. While there is little evidence for rapid changes in the average composition of the earth's atmosphere, studies by Thellier and Thellier (1959) of magnetic moments of old, fired clay bricks strongly suggest changes in the strength of the magnetic field of the earth. In France the field intensity appears to have dropped by 65 per cent during the past 2,000 years. Elsasser et al (1956) have calculated that a variation of this magnitude would cause a 2,000 year old sample to yield an erroneous age of 2,240 years.

Refinements in  $C^{14}$  measurement techniques have indeed uncovered deviations from the constant  $C^{14}$  distribution and production model. Accurate sequoia-tree-ring  $C^{14}$  measurements by Willis et al. (1960) and de Vries (1958) show somewhat irregular short term deviations of  $\pm 2.5$  per cent from the present day natural  $C^{14}$  concentration of living organisms. Similar results have been obtained by the author in work on an 1,100 year old Douglas fir from Vancouver Island (Fig. 1). The short-term fluctuations in turn are superimposed upon a gradual downward trend in the  $C^{14}$  concentration in going from 1700 A.D. to 700 A.D., in agreement with an increasing magnetic field strength (decreasing cosmic ray flux and hence a decreasing  $C^{14}$  production rate).

More pronounced is the deviation of the  $C^{14}$  concentration of samples older than 2,000 years from the present-day standard. Damon et al. (1963) found that from 2,000-5,000 years B.P. the  $C^{14}$  concentration of trees increased steadily, reaching a deviation of +6 to +8 per cent from the present-day standard. Similar results were obtained by Suess (1960) from analyses of a number of well dated tree rings and archaeological samples. In practical terms this means that a sample giving a radiocarbon age of 5,000 years is actually about 5,500 years old.

It is not possible at present to ascribe these deviations to specific causes or correct for them beyond 5,000 years B.P. Eriksson (1963) has proposed possible fluctuations in the concentration of atmospheric  $\text{CO}_2$  owing to changes in the properties of the sea, and calculated the magnitude of these fluctuations. Thus, estimated temperature and volume changes of the sea due to glaciations could account for a 1 to 2 per cent change in the  $\text{CO}_2$  content of the atmosphere, changing the  $C^{14}$  equilibrium concentration correspondingly. No matter what the causes of these fluctuations are, they are real, and therefore have to be borne in mind when applying  $C^{14}$  ages in absolute chronology.

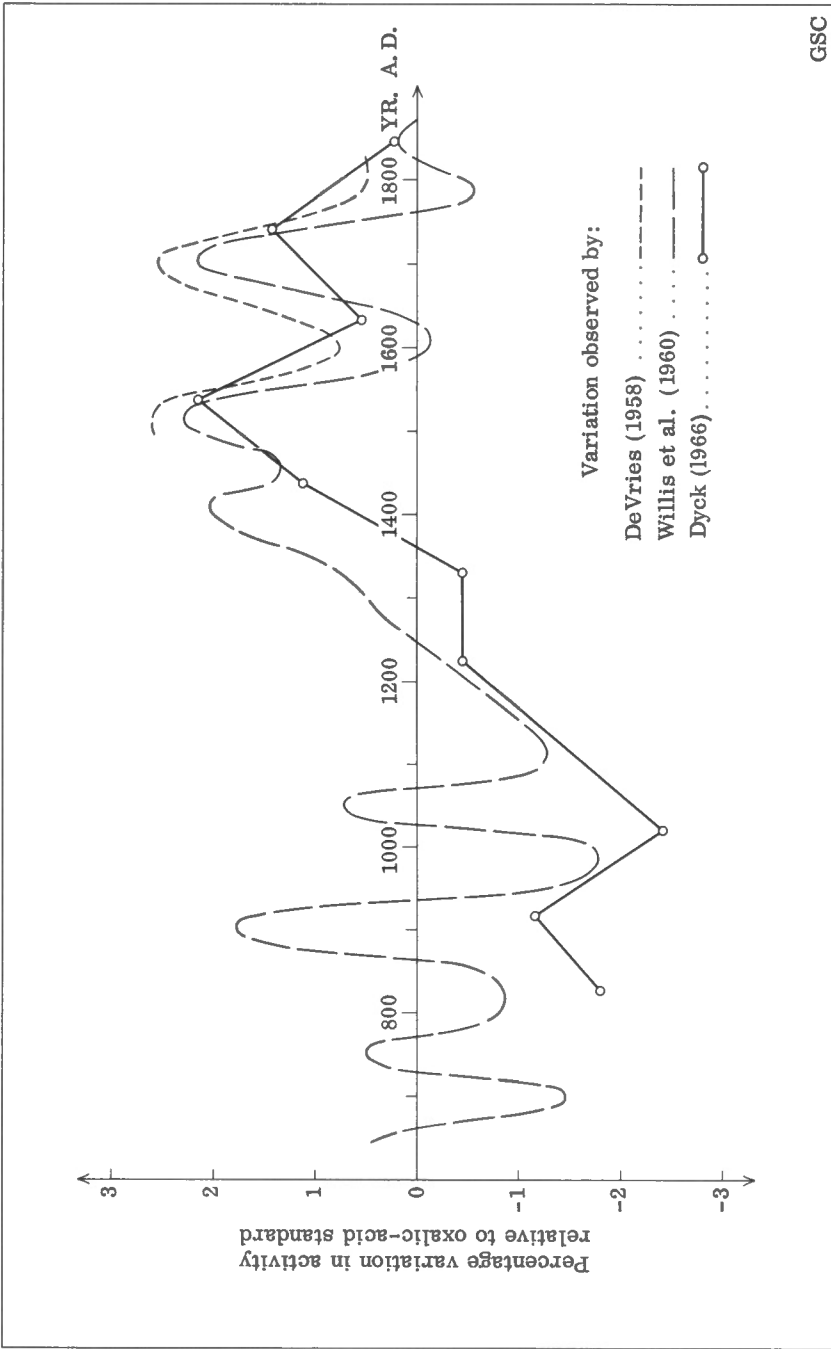


Figure 1. Secular variation of C<sup>14</sup> with time.

Since 1950, man-made  $C^{14}$  from nuclear bombs has disturbed the natural  $C^{14}$  equilibrium in the biosphere. The  $C^{14}$  concentration in Saskatchewan wheat and in leaves and grass from Champlain Lookout, Ottawa are plotted in Figure 2. As is evident, the  $C^{14}$  concentration in plants may reach twice the prebomb level, before dilution by carbon from other reservoirs reduces the  $C^{14}$  concentration in the atmosphere again. Although this artificial  $C^{14}$  will cause trouble for radiocarbon dating laboratories in the future, tracing the double humped curve through the  $CO_2$  exchange system will provide valuable information regarding residence times of carbon and water in various reservoirs and of flow rates in large underground watersheds.

Approximately 60 radiocarbon dating laboratories have been setup throughout the world since the original work by Libby in the late 1940's. While the first laboratories converted the samples to pure carbon, most laboratories today convert the samples into a gas such as  $CO_2$ ,  $C_2$ ,  $H_2$ , or  $CH_4$ .

The gas counting techniques increased the  $C^{14}$  detection efficiency from about 7 per cent to nearly 100 per cent. In the solid sample most of the ionization produced by the low-energy beta particles of  $C^{14}$  (0.154 Mev max.) is absorbed by the sample itself. Only the particles from a thin surface layer were able to escape into the sensitive parts of the detector. However, a sample in the gas phase becomes part of the sensitive portion of the detector and therefore virtually all ionizing events are recorded. In addition, the gas technique prevents air-borne radioactive particles from contaminating the sample during preparation.

Recently, liquid scintillation techniques have shown some promise as an additional age-determination technique (Tamers *et al.*, 1961; Starik *et al.*, 1963. However, at the present time  $CO_2$  is the most widely used gas in radiocarbon dating laboratories.

#### APPARATUS

Active development of the Geological Survey of Canada laboratory began late in 1959. Routine age determinations began early in 1961 using a 2-litre copper counter and  $CO_2$  as the counting gas. In 1964 a 5-litre counter was put into operation, which, when operated at 4 atmospheres extended the age range to about 54,000 years compared to 40,000 years for the 2-litre counter. By late 1965 about 450 analyses had been completed, the majority of which have been published in Radiocarbon, vols. 4, 5, 6, and 7.

The laboratory also has carried on a program of  $C^{14}$  determinations of samples of known age for the purpose of assessing the accuracy of the method and learning more about the natural and man-made  $C^{14}$  distribution and circulation in nature.

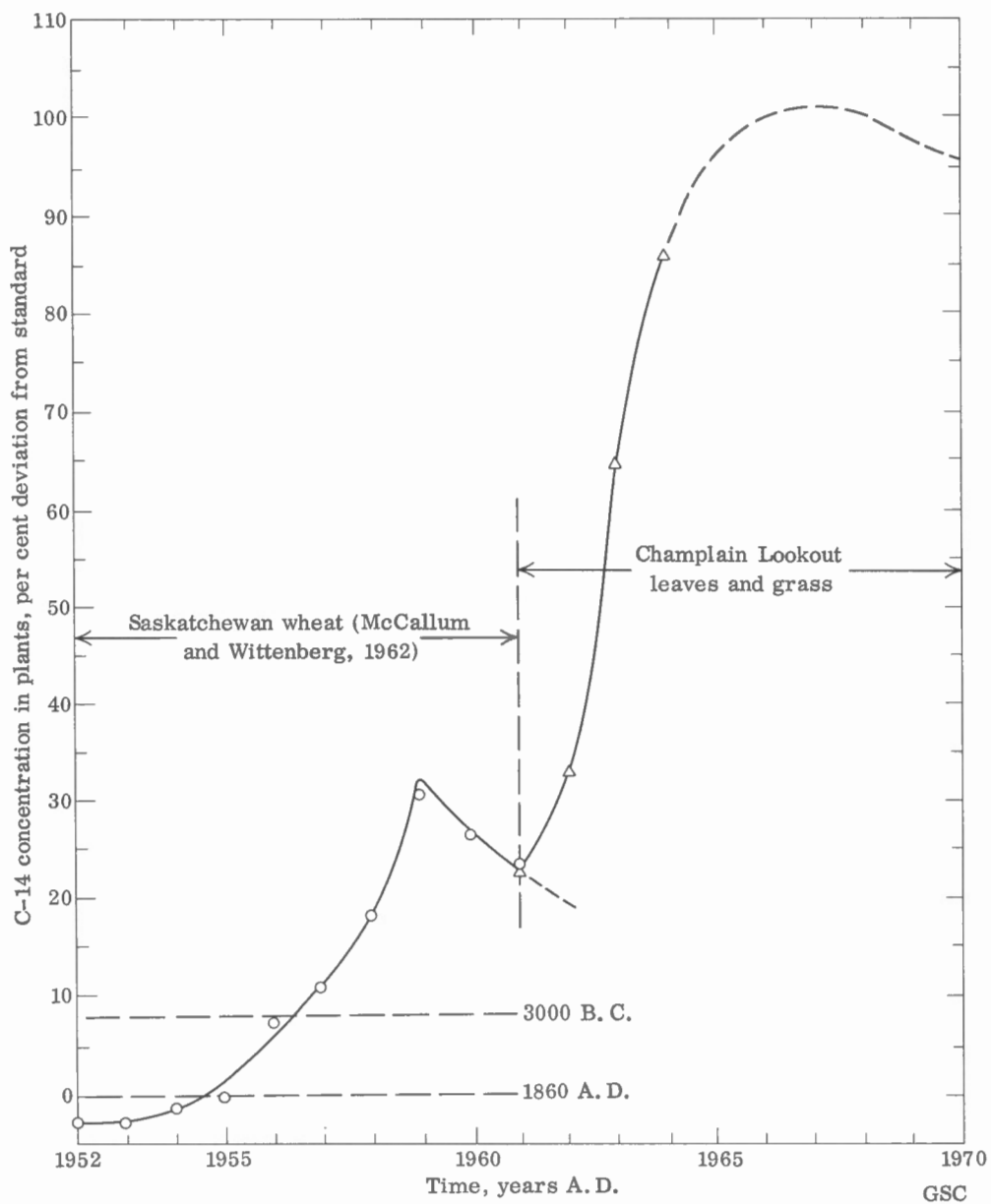


Figure 2. Variation in C<sup>14</sup> concentration in plants with time.

Apparatus and procedures described in the following pages are those used at the time of writing of this paper (1965). Minor changes in procedure have taken place continuously during the past 4 years, and hence the following accounts may not be identical to those published earlier.

### The Counting Room

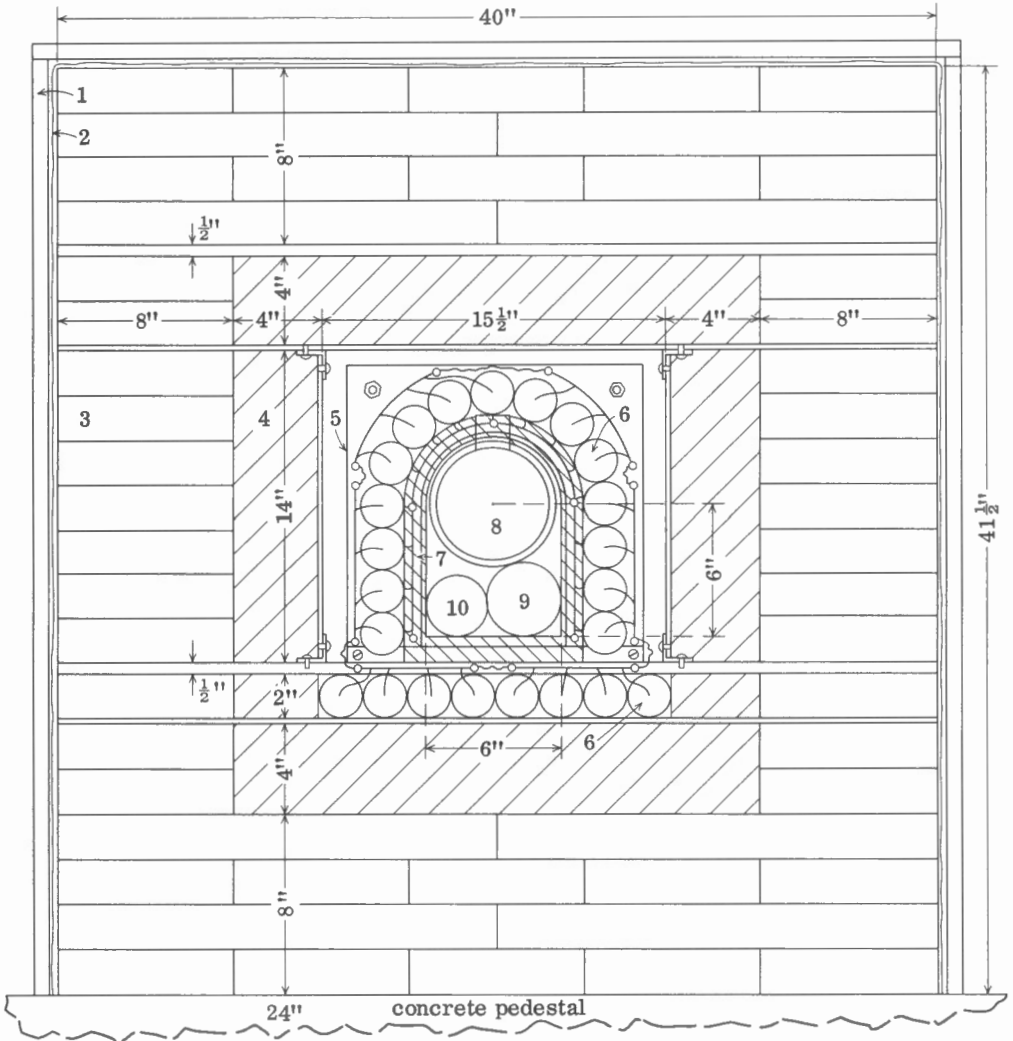
The counting room is located in the sub-basement of the eight-story Geological Survey of Canada building, thus taking advantage of the natural shielding against cosmic rays afforded by the building. Tests reveal that the cosmic ray intensity is reduced by 25-30 per cent in going from the top floor to the sub-basement. The room is air-conditioned, and an electrostatic air cleaner was installed in 1962 to prevent the accumulation of long-lived radioactivity in the room.

### The Counter Shield

The counter shield comprises 8 inches of cast iron, 4 inches of paraffin, 23 cosmic ray guard tubes, and 1 inch of mercury. To prevent the accumulation of dust inside the castle by thermal convection currents, the whole assembly is wrapped in polyethylene and covered with plywood. Provision is made for access through openings at the front of the castle. A cross-sectional view of the front of the shield, without the door and front dust covering is shown in Figure 3. Figures 4 and 5 show some additional constructional details of the shield and counter arrangements within.

The cast-iron layer consists of bricks and slabs measuring 2"x4"x8" and 2"x8"x20" respectively, and shields the sample counters against gamma radiation emanating from brick walls and concrete floors. The 4 inch paraffin layer was placed inside the iron in order to slow down and absorb neutrons produced by cosmic rays in the atmosphere, building, and iron shield. For practical reasons no paraffin was put at the front. The 48"x15 1/2"x16 1/2" space inside the iron-paraffin assembly provides enough room for 3 sample counters of 5 litre, 2 litre, and 1 litre capacity, respectively, 4 preamplifiers, a stainless steel vessel containing 550 lbs of mercury, and a ring of 23 cosmic ray tubes. The mercury vessel is constructed from 30 mil stainless steel and provides a 1 inch thick by 36 inch long layer of mercury as an additional  $\gamma$ -ray shield for the sample counters. A reduction of approximately 0.5 c/m in the background of the 2-litre counter was obtained after filling the vessel with triply distilled mercury.

The castle door consists of a steel-plate box, 32"x32"x8 1/2", filled with 2"x4"x8" iron bricks, and is supported and guided by one v-shaped and one flat castor-and-rail combination. Positive horizontal motion is achieved by a rack and pinion mechanism.



REFERENCE

- |                                  |  |
|----------------------------------|--|
| 1. 3/4" plywood                  | 6. Guard counters                      |
| 2. Polyethylene sheet            | 7. Hg vessel, 1" x 36" stainless steel |
| 3. Cast iron                     | 8. 5L counter                          |
| 4. Paraffin                      | 9. 2L counter                          |
| 5. Plastic guard counter support | 10. 1L counter                         |

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Figure 3. Cross-section of the radiocarbon counter shield.



Figure 4. Electronics and castle.

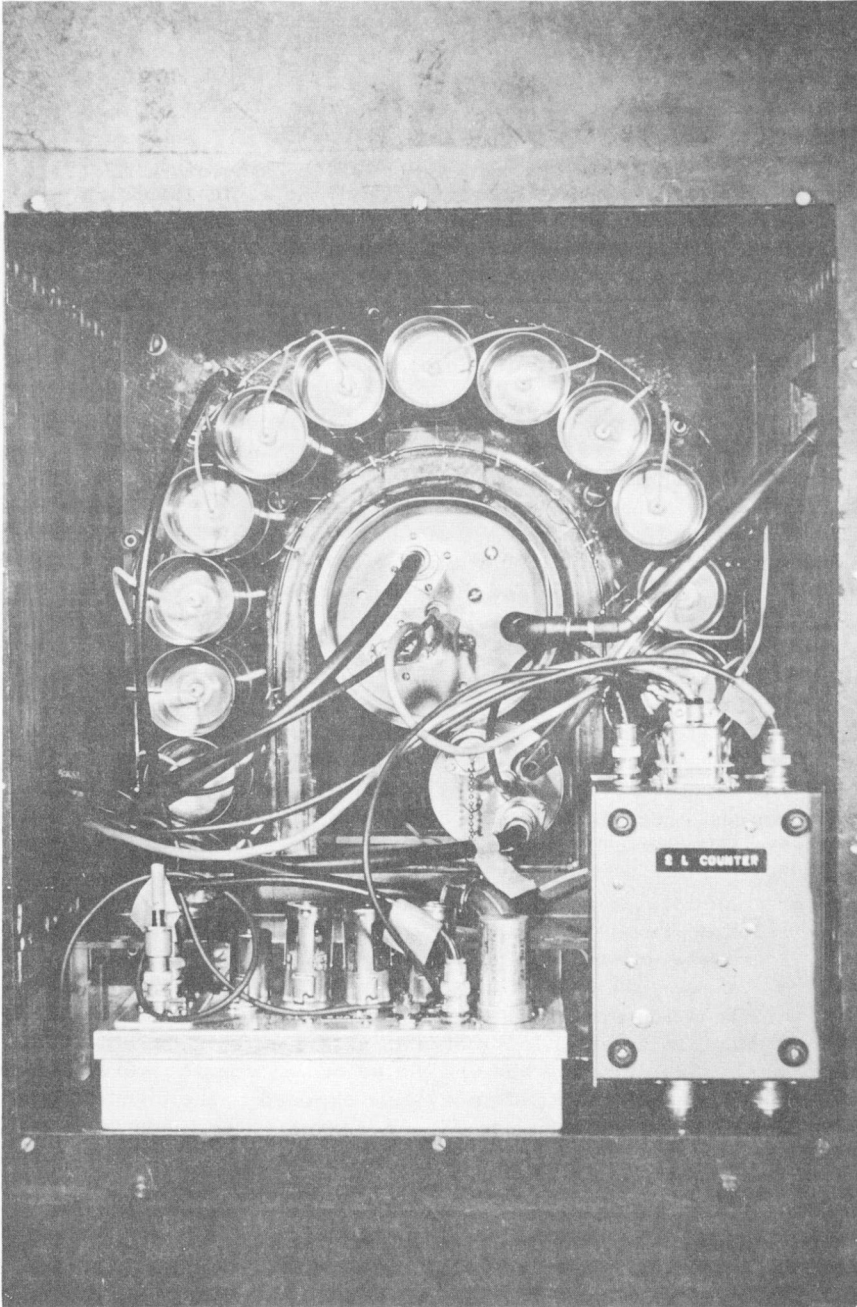


Figure 5. Inside the castle.



### The Guard Counters

The cosmic-ray guard contains 23 counters, which are 40 inches long by 2 inches in diameter and have an active length of 38 inches. The copper cathodes are fitted with alumina insulators. The first set of tubes, purchased from N. Wood Counter Laboratories, were of the Geiger-Mueller type. Arranged inside the castle as shown in Figure 3, they registered a counting rate of approximately 2,400 c/m. When the first set of tubes deteriorated a set of 'Long-Life' proportional tubes from the same supplier was installed. This change brought about an 8 per cent reduction in the background rate of the sample counters and increased the guard counting rate to 2,750 c/m.

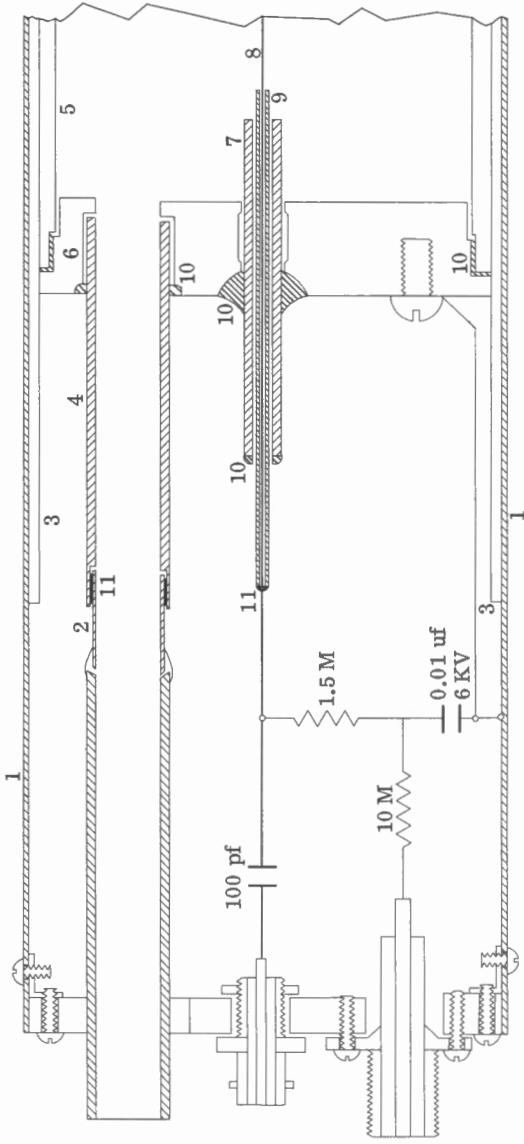
### The Sample Counters

A 2-litre (2 L) proportional counting tube was designed and fabricated in 1960 and put into operation early in 1961. A cross-sectional view of the service end of the counter is shown in Figure 6. The inside wall of the counter was cleaned by machining a 30 mil layer and rinsing with distilled water and acetone prior to assembly. Assembly was completed as soon as possible after machining to avoid undue exposure of surfaces to airborne radioactive particles. The copper end plates and quartz insulators were glued in place with araldite (Walden W-103 adhesive). The 1/16-inch teflon insulation between the counter cathode and the 1/32-inch stainless steel shield permitted safe operation of the counter cathode at potentials other than ground.

The more significant performance characteristics of the counter are given in Table I. Figure 7 shows the relationship of counting rate vs applied voltage at various pressures. The counter is operated routinely at a pressure of 2 atmospheres where the maximum dating limit is 40,000 years, using the 4 sigma criterion.

After considerable testing and modification, a 5-litre (5 L) counter, designed to operate at pressures of up to 5 atmospheres, was put into operation in 1964. A cross-sectional view of the counter is shown in Figure 8.

Originally teflon insulators were used. However, rapid poisoning of the counter-filling gas by volatile substances in the teflon necessitated the substitution of quartz insulators. The end plates of this counter were welded in place, thus reducing the amount of epoxy glue exposed to the counting chamber. The sealing washer in the front-end insulator was made from 16th century lead because of its lower radioactive lead content. Procedures and precautions similar to those for the 2-litre counter were used in the cleaning and assembly. Table I lists some of the more important test data obtained with this counter, and in Figure 9 the relationship of counting rates vs applied voltage is shown. It is interesting to note that in both 2 L and 5 L counters a relative shift in the knees of the meson and  $C^{14}$  plateaux takes place with a



REFERENCE

- |  |                               |
|--|-------------------------------|
| 1. 1/32" stainless steel grounded shield     | 7. 7mm x 2 1/4" quartz        |
| 2. 1/2" Kovar                                | 8. 2mil stainless steel anode |
| 3. 1/16" Teflon                              | 9. 1/8" O.D. copper           |
| 4. Brass adaptor                             | 10. Epoxy glue                |
| 5. 3" O.D. copper tube 1/8" thick x 20" long | 11. Soft solder               |
| 6. 3/4" Copper end plate                     |                               |

GSC

Figure 6. Cross-section of service end of 2 litre counter.

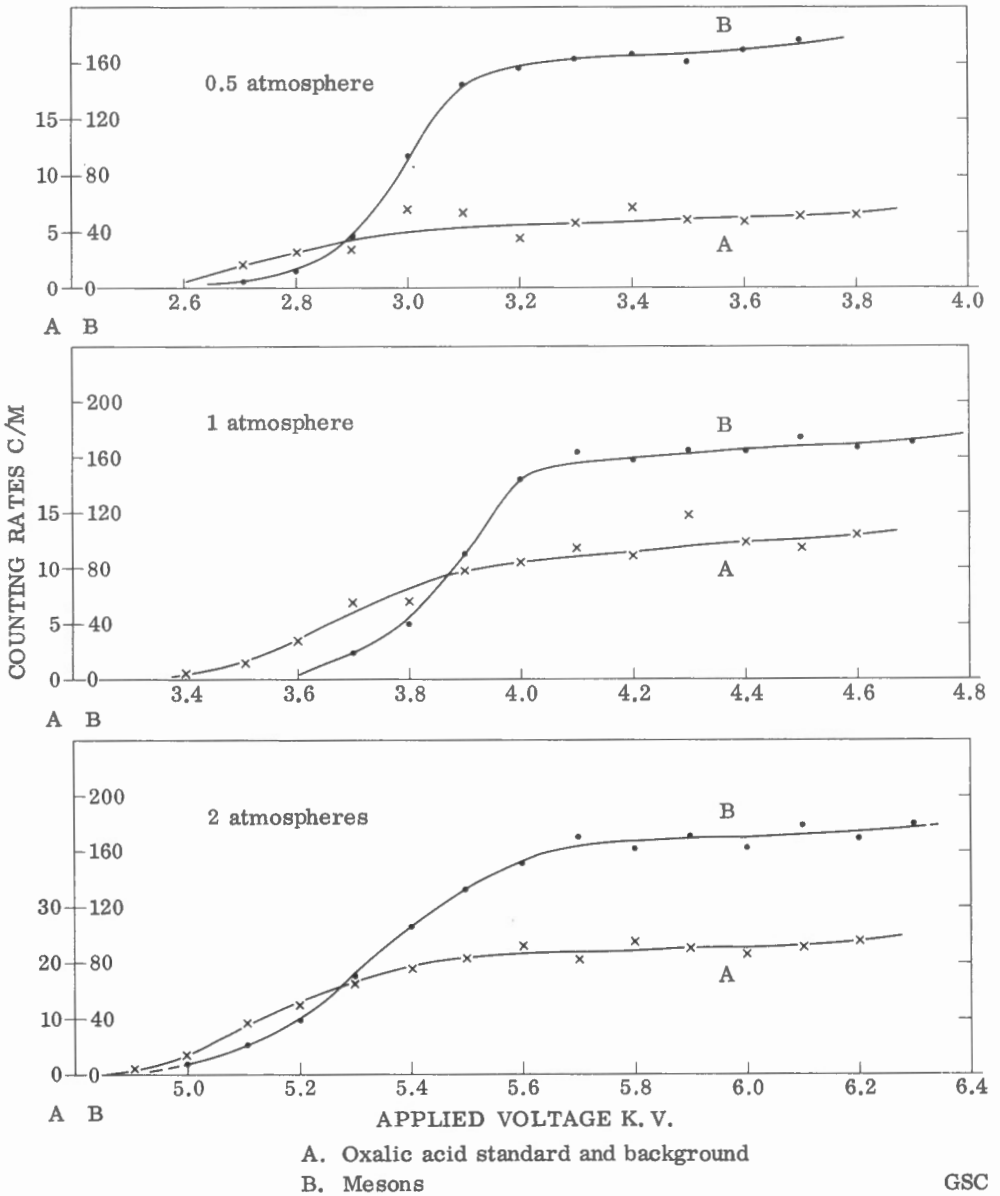


Figure 7. 2 litre counter plateaus.

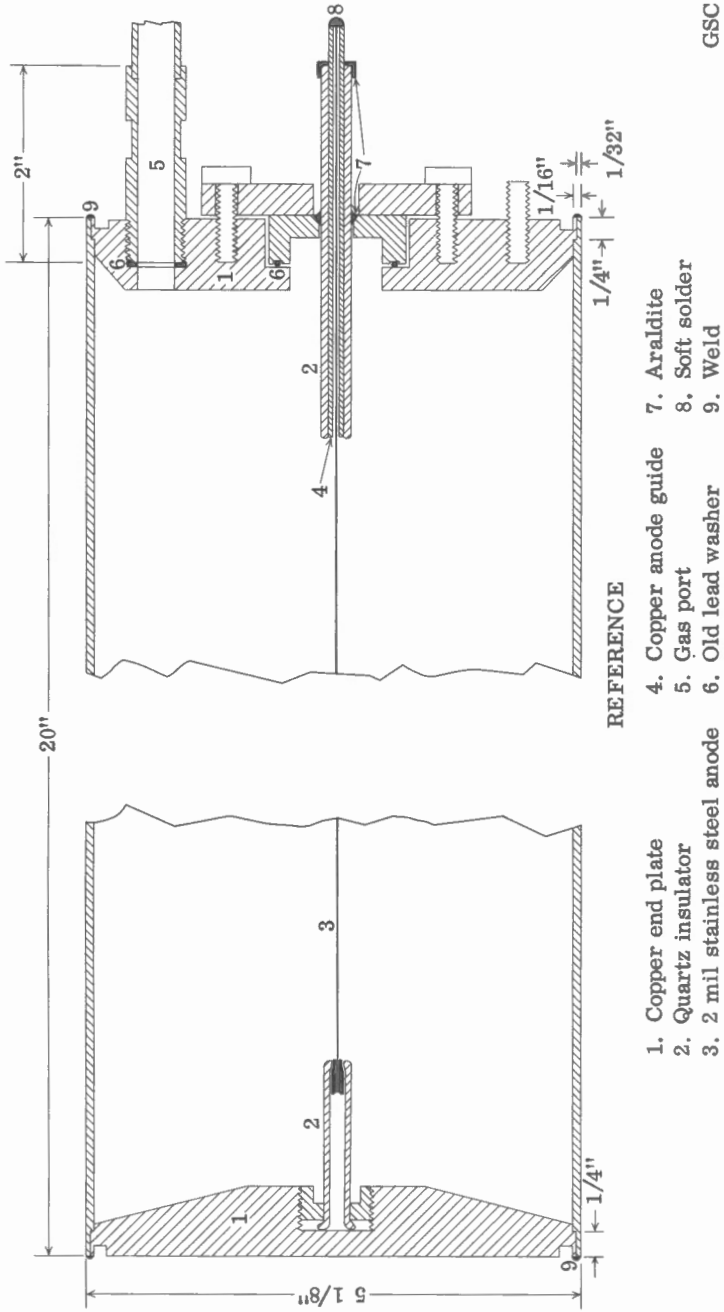
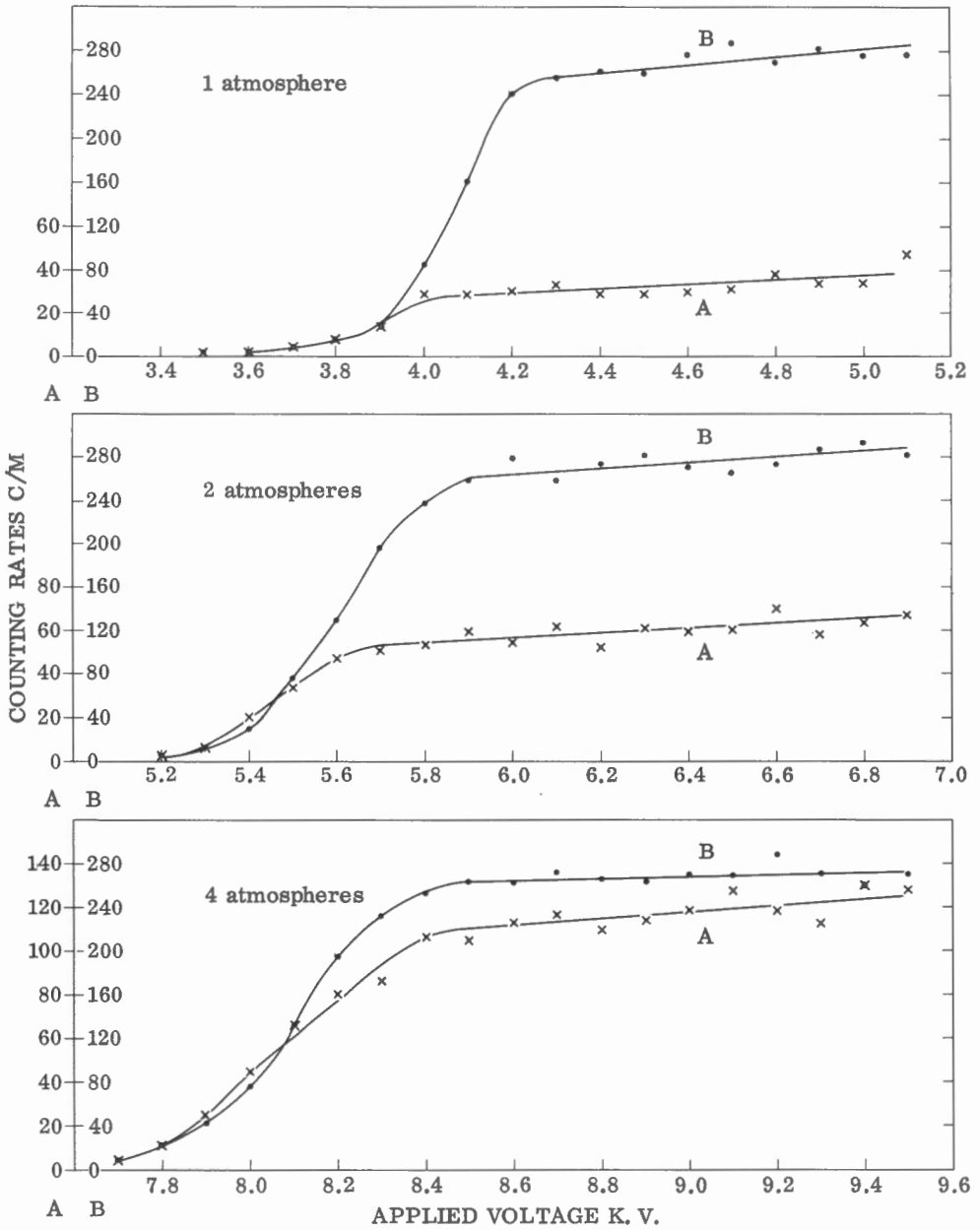


Figure 8. Cross-section of 5 litre counter.



A. Oxalic acid standard and background  
B. Mesons

GSC

Figure 9. 5 litre counter plateaus.

TABLE I  
Counter Characteristics

Counter	Counter volume Litres*	Operating pressure atm.	Operating voltage k.v.	Back-ground (B) c/m	Standard (No) c/m	Mesons c/m	Plateau Slopes**		Figure of Merit †
							Meson	C14	
2 L	1.86 (1.73)	0.5	3.3	1.18 + .07	5.3 + .1	164	1.9	3.1	4.1
		1.0	4.3	1.31 + .03	10.3 + .2	165	1.2	2.6	7.6
		2.0	5.8	1.40 + .04	20.1 + .1	165	0.6	1.7	14.2
5 L	5.68 (4.93)	1.0	4.6	2.30 + .03	28.4 + .1	269	1.2	3.6	15.7
		2.0	6.3	2.53 + .04	56.8 + .5	271	0.6	1.4	28.0
		4.0	8.9	3.10 + .05	111.0 + .4	268	0.4	1.0	49.5

\* Value in brackets is sensitive volume of counter i. e. volume between anode sleeves.

\*\* The plateau slopes are expressed in % per 100 volts and were measured over a 500 volt interval.

Meson = total rate - (sample + background rates)

C14 = oxalic acid standard + background rates.

† The figure of merit was calculated using the following expression

Figure of Merit =  $C \cdot V \cdot \text{No} / B$  where,

C = counting efficiency  $\approx .90$  (estimated)

V = volume efficiency =  $\frac{\text{sensitive vol.}}{\text{total volume}}$

= .93 for 2 L counter

= .87 for 5 L counter

No = 0.95 x net counting rate of NBS oxalic acid standard

B = background counting rate.

change in pressure. The fractional counting rates of mesons and  $C^{14}$  expressed as per cent, vs applied voltage, are plotted in Figure 10, and it is evident that the average number of ion pairs produced per  $C^{14}$  particle is somewhat greater than that for mesons in both counters. Two further observations can be made from the graphs in Figure 10. As the pressure increases, the specific ionization for mesons increases as indicated by a gradual voltage shift of the meson peaks with respect to the  $C^{14}$  peaks. This must be so, because the mesons lose only a very small portion of their energy in the counter, whereas the  $C^{14}$  betas lose all their energy in a few cm, and hence the amount of ionization produced by the mesons will depend greatly on the number of collisions they make in traversing the counter. The number of collisions in turn depends on the density of the gas. Secondly, a general broadening of the peaks and lengthening of the low energy tails with an increase in pressure indicates a shift in the plateau towards the region of limited proportionality where the gas amplification factor for the higher energy particles is suppressed relative to the lower energy particles.

The data in Table I show that the background increases somewhat with increasing pressure, but the plateau slopes improve. The slight departure from linearity in the counting rate of the standard with increased pressure could be due to the arbitrary choice of the operating point.

The 5-litre counter has been operated successfully at 4 atmospheres pressure, giving a maximum age limit of 54,000 years.

### The Electronic Equipment

The basic electronic equipment consists of a transistorized Sharp Low-Beta unit, a Baird-Atomic model 255 preamplifier for the guard counters, Fluke high voltage supplies, an assortment of decatron scalers for totalizing counts, and a ten pen Esterline-Angus Operation Event Recorder, which provides a permanent and continuous record of the output of the various scalers. The basic electronic units are shown in the schematic diagram of Figure 11. Additional details of the main electronics and preamplifiers are shown in Figures 4 and 5. A typical recording of the counting rates is presented in Figure 12. Signals from selected decatron outputs are fed into univibrator type circuits, which activate the relay-driver pen mechanisms. The recording consists of blips made by the pens on the chart, which moves at a constant known speed. Each blip represents  $10n$  counts where  $n = 1, 2, 3, \dots$  etc. corresponding to the 1st, 2nd, 3rd  $\dots$  etc. decatron output, which is selected as desired, depending on the counting rate of the particular channel. Thus large counting rate fluctuations, power failures, electronic break-downs, etc. may be detected more readily. The recorder has been most useful in determining the reliability (statistical variation) of weekend counts, eliminating the need for a second count for samples counted over a weekend. The counts recorded by pen 1 to 7 (from left to right in Figure 12) represent the guard,

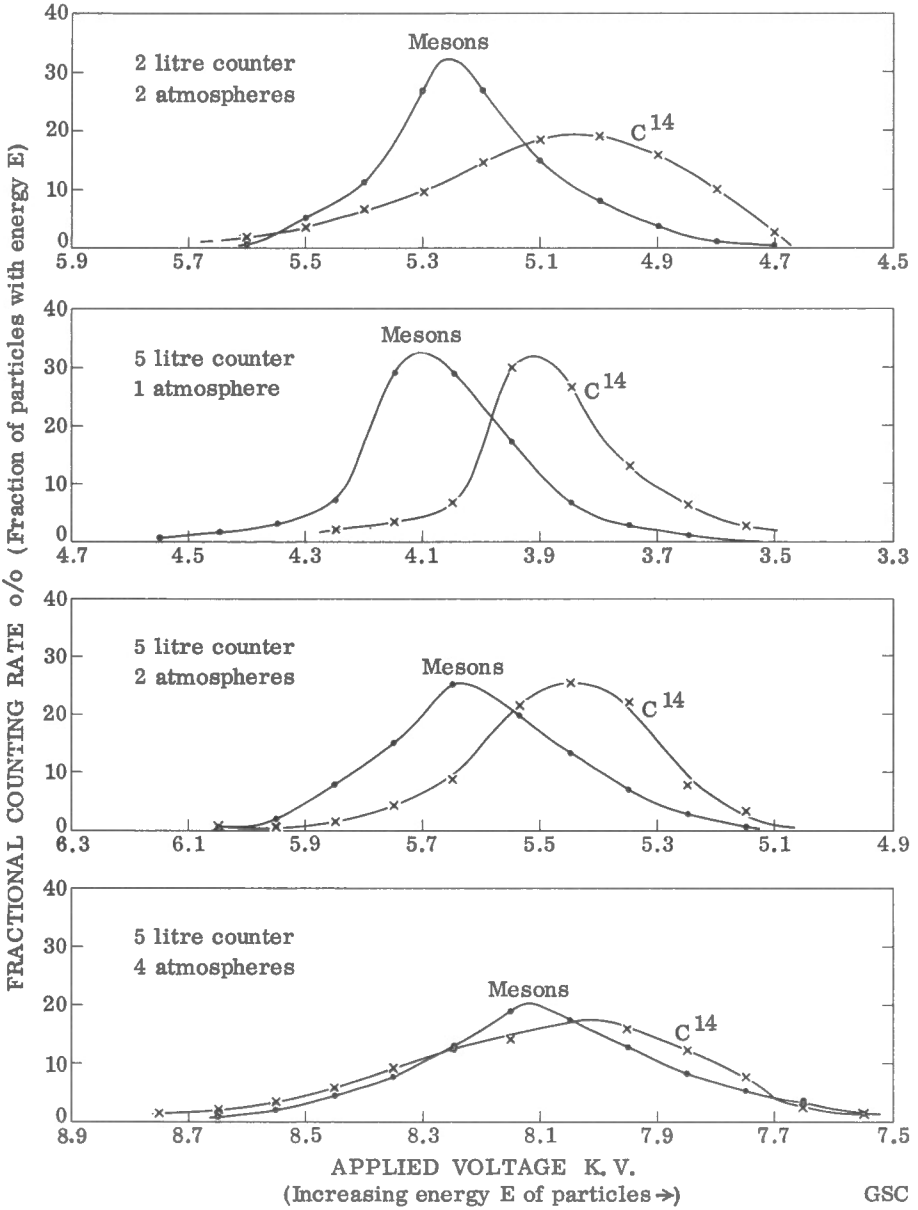
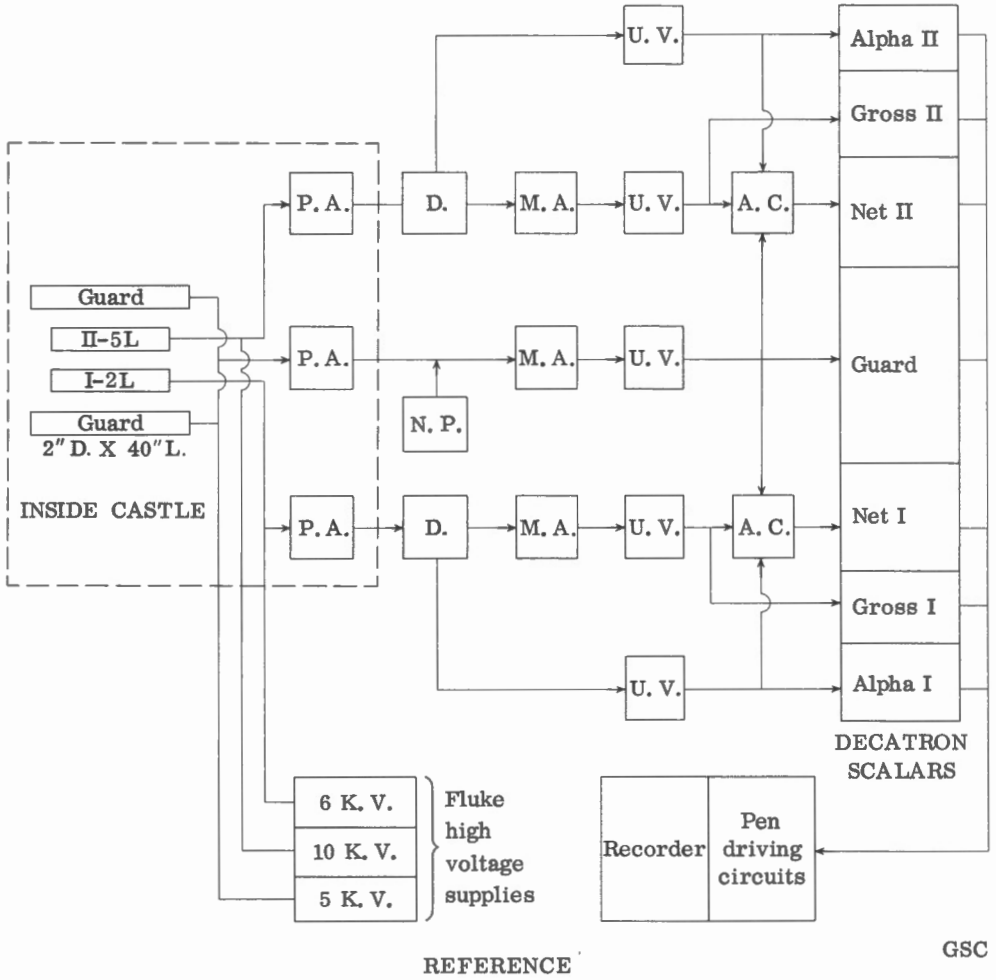


Figure 10. Fractional counting rates vs applied voltage.





GUARD = 23 proportional counting tubes  
 II - 5L = 5 litre sample counter  
 I - 2L = 2 litre sample counter  
 P. A. = Preamplifier  
 D. = Discriminator

M. A. = Main amplifier  
 N. P. = Noise pick up  
 U. V. = Univibrator  
 A. C. = Anticoincidence circuit

Figure 11. Electronics flow diagram.

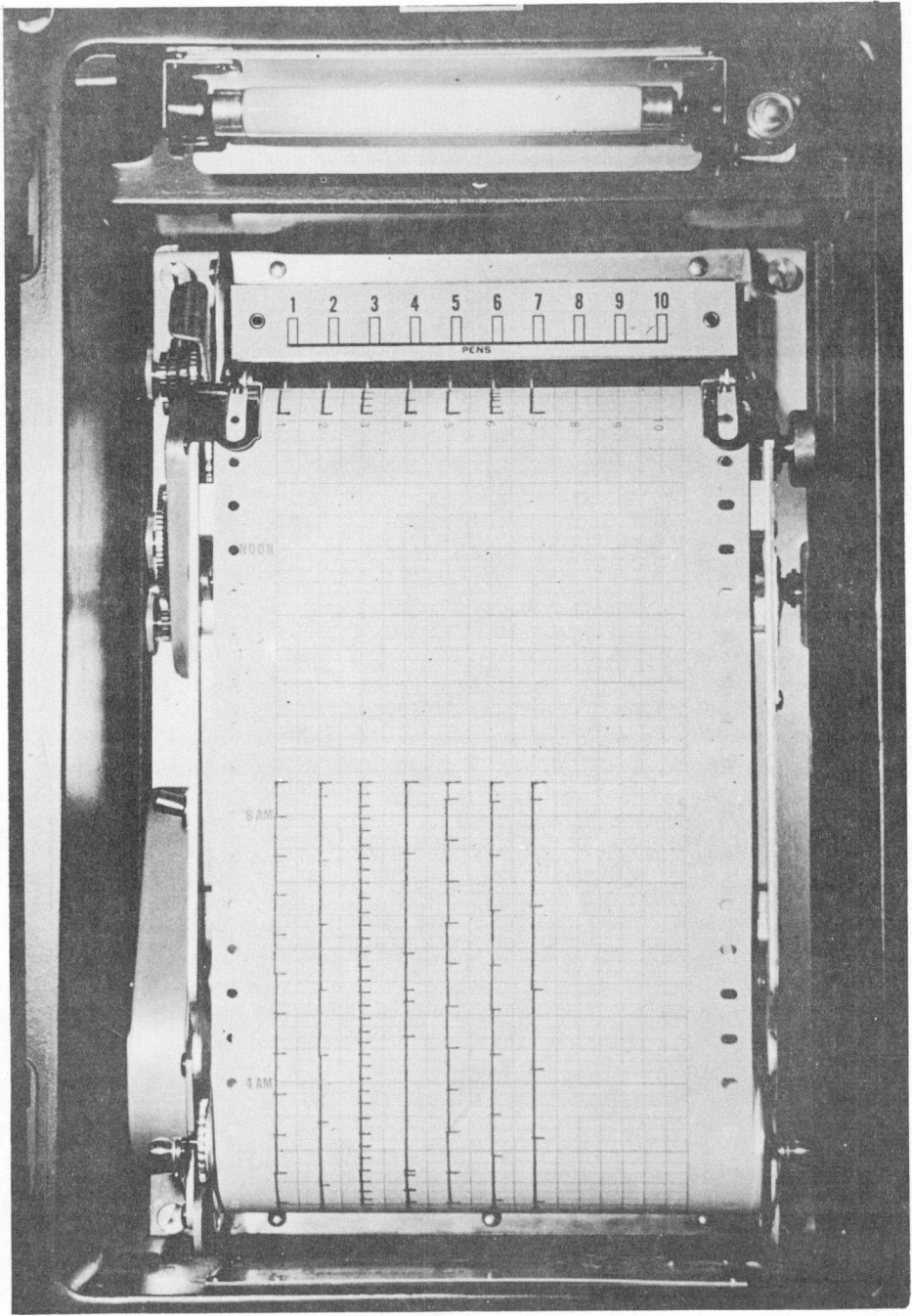


Figure 12. Esterline-Angus chart recording.

2 litre gross, 2 litre net, 2 litre alpha, 5 litre gross, 5 litre net, and 5 litre alpha channel rates, respectively.

The built-in alpha discriminators of the Sharp unit could not be used to full advantage for the detection and correction of radon contamination in the samples because of the high gain and low clipping limit (8 volts) of the preamplifiers, and the fact that the operating point had to be in the region of limited proportionality in order to obtain high efficiency  $C^{14}$  beta counting.

### The Sample Preparation System

The  $CO_2$  preparation and purification system is shown in schematic flow diagram of Figure 13 and in Figure 14. The legend of Figure 13 describes most of the components adequately, but there are a few units that require additional clarification. Trap 1 is used to absorb traces of  $CO_2$ , which could be present in commercial tank oxygen, and also serves to give a rough indication of the oxygen flow rate. The sample combustion tube is made of clear 2 mm vycor, 1 1/4" O.D. x 36" long with removable rubber stoppers and ceramic heat reflectors at each end. A stainless steel tube 1 1/8" O.D. x 12" long, cut in half along its longitudinal diameter, is used as a sample combustion boat. Trap 5 was used to absorb  $SO_3$  and collect the water of combustion. The first  $AgNO_3$  trap is an ordinary glass tube bubbler, the second has a coarse fritted glass gas-dispersion tube. The fritted glass provided for dispersion of the gas and hence more efficient absorption of halides by the  $AgNO_3$ . Both  $CrO-H_2SO_4$  bubblers were of the fritted glass type and have been found to be good sulphur oxide scrubbers. The  $CaSO_4$  and dry ice-acetone traps remove most of the water from the combustion gases. Removal of additional trace quantities of water is achieved with the copper oxide wire trap 25 (on Fig. 13) chilled with a dry ice-acetone mixture and the  $420^\circ C$  copper wire trap 24. The Pt-asbestos and Ag-wool in 10 are used for the removal of sulphur oxides and halides. Although most samples do not need this trap, some discolouration of the Ag-wool during the past four years indicates that it has served a purpose. Trap 11a, which is made from a 1-litre round-bottom flask, presents a large surface area, thereby making it an efficient  $CO_2$  collector at liquid  $N_2$  temperatures, without undue trapping of the excess oxygen usually present during sample combustion. For several years traps 11a and 11b were also used in the removal of radon and other non-condensable gases such as  $O_2$ , employing the principle of fractional distillation described by de Vries (1957). Radon removal trap 20a was installed later. It consists essentially of two concentric copper tubes with a 4 mm annulus between them, the innermost tube (41 mm O.D.) forming part of the vacuum system and the outer tube (49 mm I.D.), which is kept in liquid nitrogen during the radon removal, providing the 4 mm air space and hence the proper temperature gradient for the inner tube. The final purification step consists of passing the gases through hot copper wire trap 24 ( $CuO$  wire reduced to  $Cu$  with  $H_2$ ). Commercially available copper wool and household scouring pads made of copper mesh were found to be quite dirty and ineffective in this purification step. The 5-litre

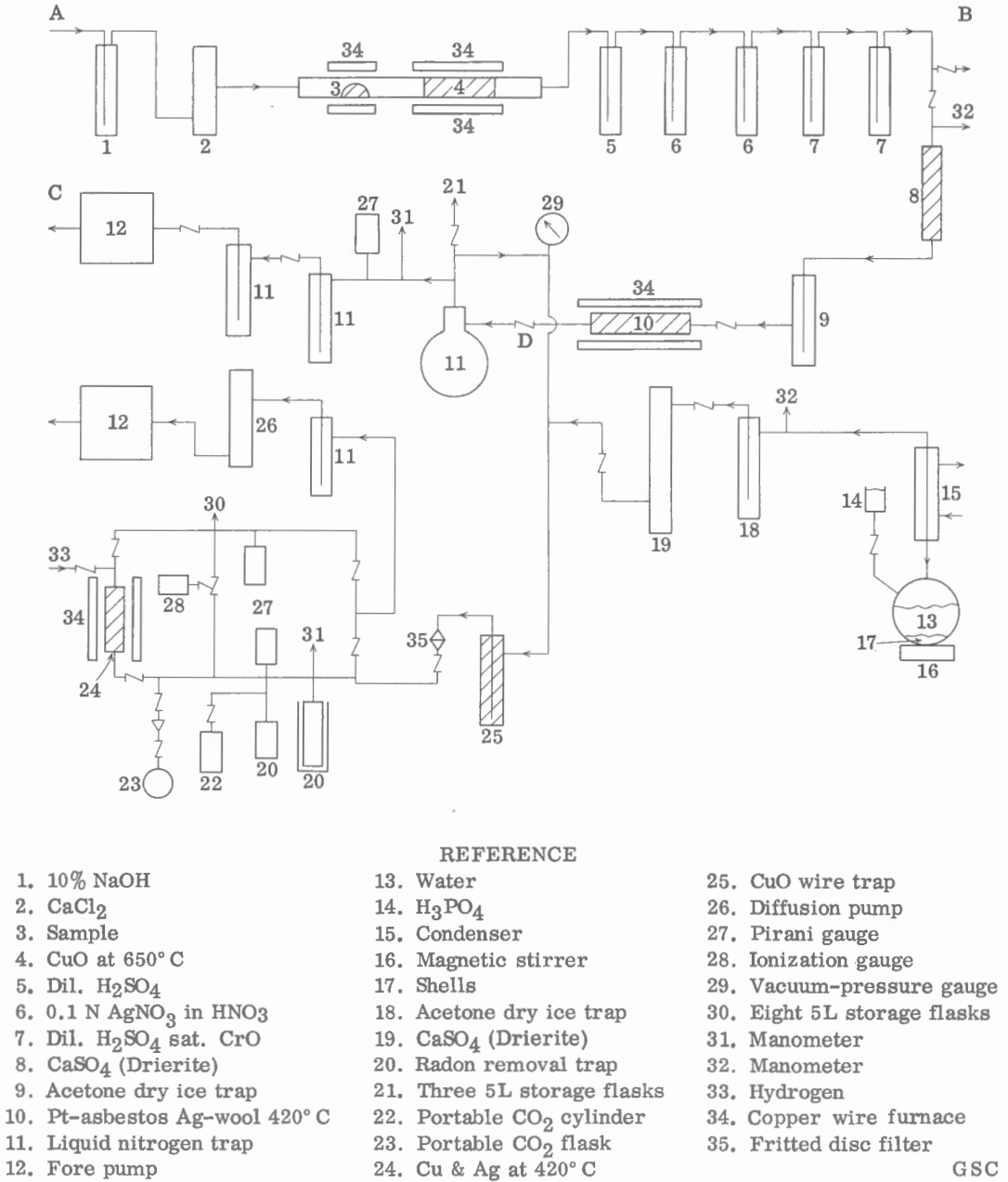


Figure 13. Carbon dioxide preparation and purification system.

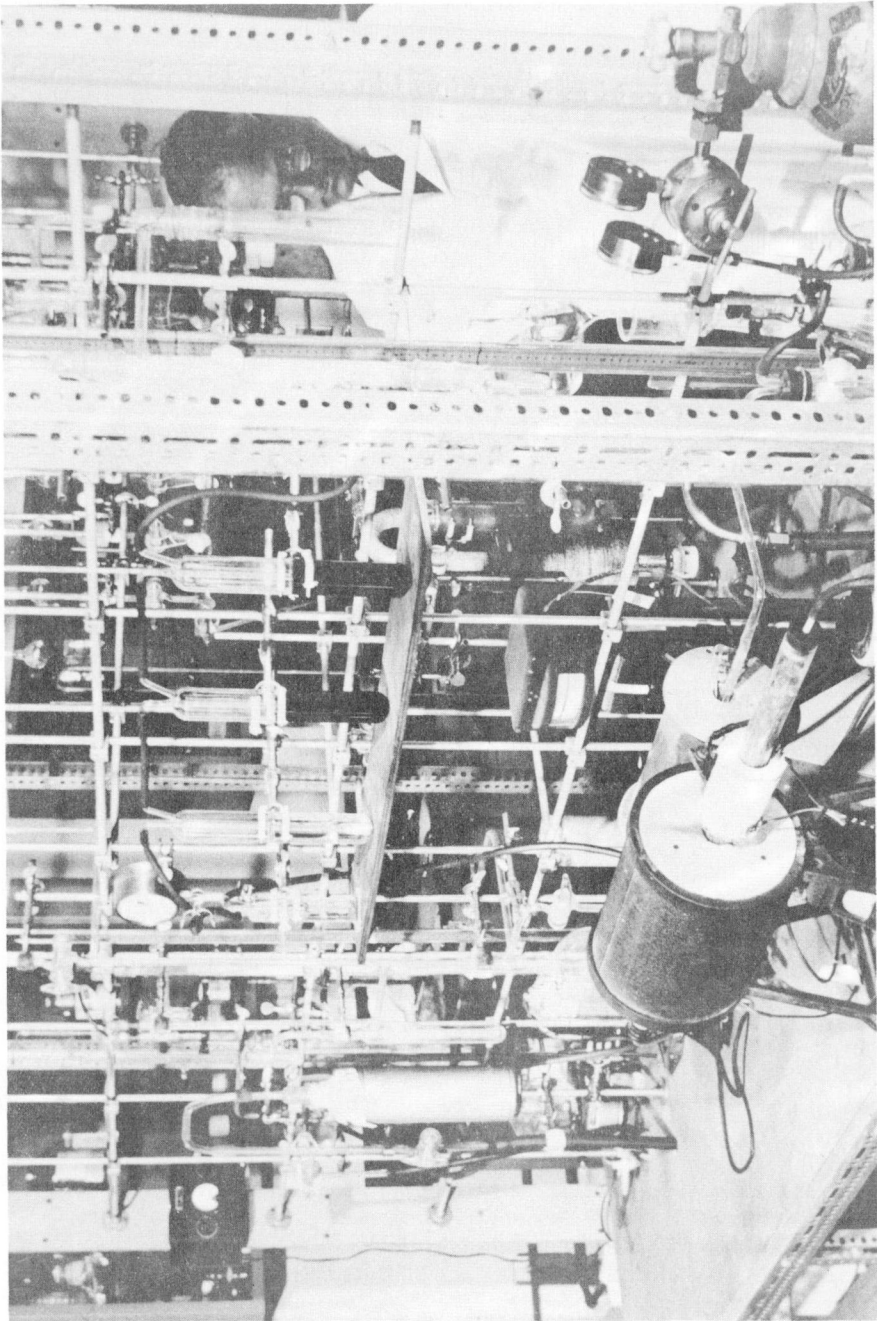


Figure 14. Sample preparation line.

glass flasks (30 on Fig. 14) and the portable steel cylinders (22 on Fig. 14; Hooke cylinder #6HS300 with Hooke #256A valve) provide for storage of 30 samples. Samples containing large quantities of radon may require two to four weeks storage to allow for radon decay in addition to the usual radon removal procedure.

All connections between points A and B in Figure 14 are made with high quality rubber tubing. This section of the system is therefore operated at or slightly above atmospheric pressure. The remaining lines are of pyrex with vacuum-cup stopcocks to permit operation under vacuum as well as at pressures above atmospheric. Section B to C is evacuated with a fore pump only, giving a vacuum of  $10^{-3}$  mm Hg. The sample storage and final purification section is evacuated with a fore pump and a mercury diffusion pump. A vacuum of  $10^{-6}$  mm Hg may be achieved in this section, but routine operation at  $10^{-4}$  mm Hg gave satisfactory results.

### The Counter Filling System

Portions of the 2-litre and 5-litre counter filling systems are shown in Figures 15 and 16 respectively. The 2-litre filling system made of glass, provides for storage of 10 samples in 5-litre flasks. It is also equipped with a radon removal trap and hot copper furnace similar to that in the sample preparation line, to facilitate the repurification of a sample if required. The sample counters are permanently attached to the filling systems. Pressures in the 2-litre counter, of up to 2 atmospheres, are measured with a Hg manometer. A Veeco ionization gauge is used to monitor the vacuum. The 5-litre counter filling line is constructed from 1/2" O.D. hard copper tubing and Veeco valves. Samples for this line are transported and stored in Hooke high pressure cylinders, which are connected to the filling line using a modified Swadgelock coupling and a teflon washer. Pressures above one atmosphere are measured with a Heise, Bourdon tube-gauge with a 12 inch diameter dial. At one atmosphere it gives readings reproducible to within 0.2 per cent compared to a mercury manometer. Vacuum is measured with a Rochester Dynamics cold cathode discharge gauge.

## PREPARATION AND MEASUREMENT OF THE SAMPLE

### Sample Pretreatment

Labelling, recording, physical examination, removal of extraneous matter such as rootlets in charcoal, or limy silt in sea shells, and drying of samples ( $\sim 85^{\circ}\text{C}$ ) not processed immediately upon submission to the laboratory, are routine operations to which all samples are subjected.

Wood samples are scraped on the outside, cut into splinters with sides smaller than 1/4 inch, treated one half to one hour each with hot 1 per cent Na OH, hot 2N HCl, hot water, and then dried. Charcoal and peat samples with a fibrose structure are given the same chemical treatment as wood. However, some peats are sufficiently soluble in base that only a 10 to 15 minute cold base leach is practical. The base leach is completely omitted from the pre-treatment of all soils, some peats, and some gyttjas.

Sea shells are cleaned with a stiff brush and water before removal of 10 to 40 per cent of the outer layers with dilute HCl. The amount removed depends on the physical condition of the shell.

The organic fraction of bones, mainly collagen, is extracted by dissolving crushed bone in 2-4 N HCl and passing the solution through a sintered glass filter. Usually dissolution is carried out in the shell apparatus 13-19 (Fig. 13) so that the CO<sub>2</sub> from the bone carbonate can be collected and dated also.

No chemical pretreatment is carried out on the background material, Pennsylvania anthracite and Precambrian limestone, and on the N.B.S. oxalic-acid standard. Contemporary samples such as leaves, and tree rings of known age are generally not pretreated.

The following quantities of dry raw materials were usually found to give sufficient pure CO<sub>2</sub> gas to fill the 2-litre counter to 2 atmospheres pressure:

Charcoal	5 grams
Wood	8 grams
Peat	15 grams
Shells	28 grams
Soils	100-500 grams
Bones	300-1000 grams

However, much smaller samples have been prepared on occasion and mixed with background CO<sub>2</sub> for the C<sup>14</sup> measurements.

#### Combustion and Purification of Organic Samples

A weighed amount of treated sample material is placed in a stainless steel boat and placed in the combustion tube. Oxygen is passed through the system A-B (see Fig. 13) for approximately 10 minutes to flush out air and traces of CO<sub>2</sub> from the previous run. The then O<sub>2</sub> flow is rerouted through the evacuated system B-C and exhausted via the fore pump. The desired gas flow rate is maintained by properly adjusting the pressure reducing valve on the O<sub>2</sub> cylinder and the stopcock (D on Fig. 13). Following ignition of the sample traps 11a and 11b are cooled with liquid nitrogen in order to

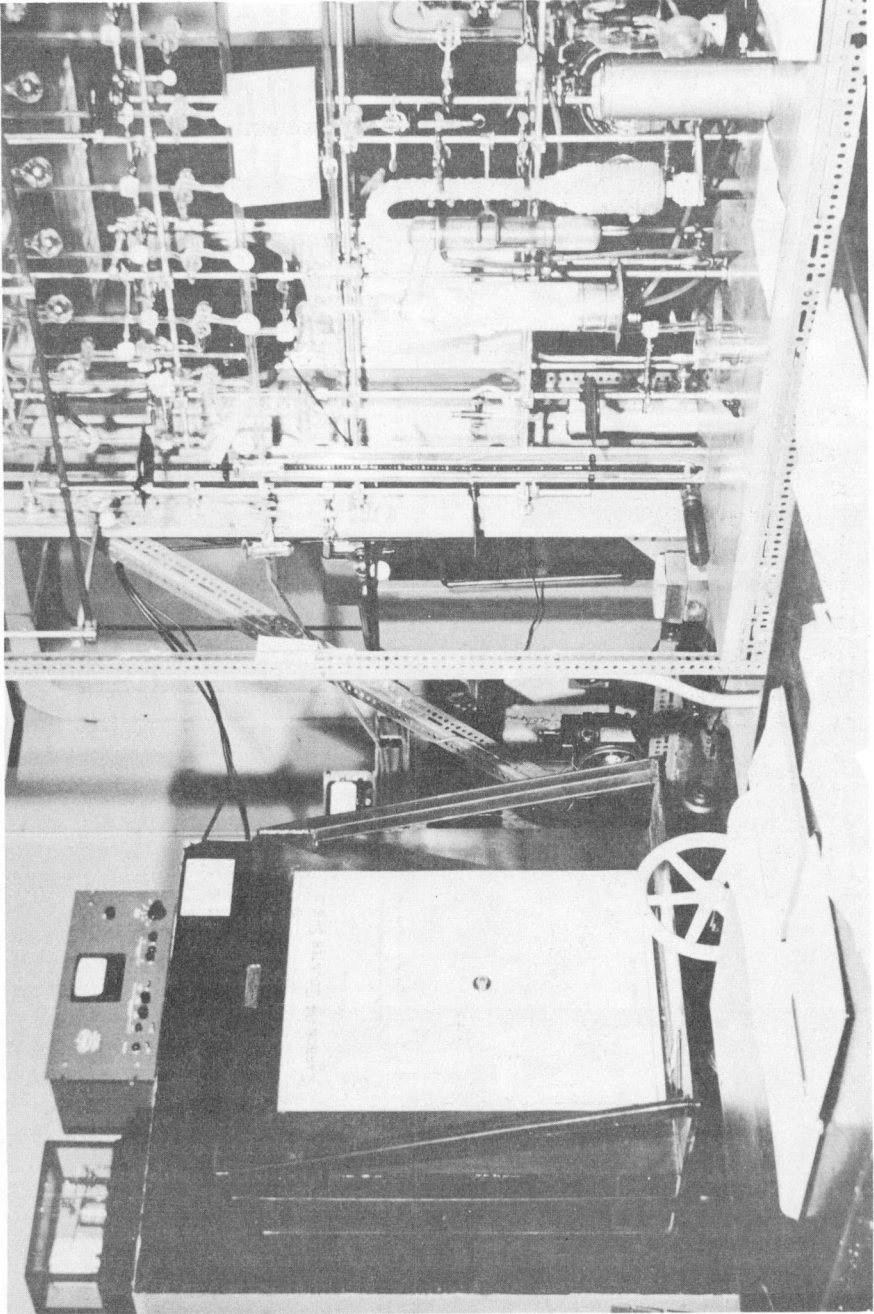


Figure 15. 2-litre counter filling line.



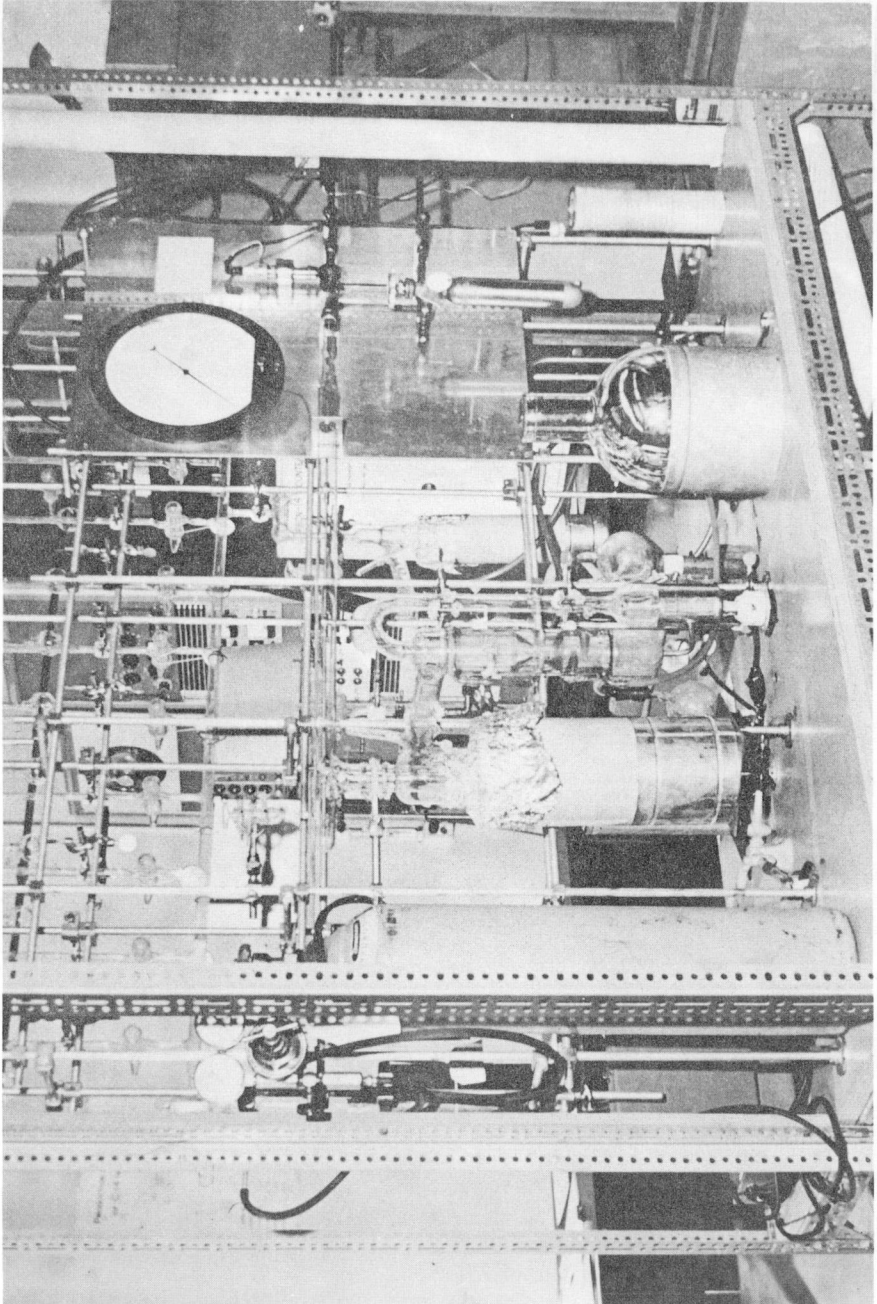


Figure 16. 5-litre counter filling line.

condense the  $\text{CO}_2$ . In order to avoid condensation of  $\text{O}_2$  with the  $\text{CO}_2$  the pressure in these traps is not permitted to exceed 5 cm Hg during combustion. When the sample is completely burned the  $\text{O}_2$  flow is stopped, stopcock D turned off, and the excess  $\text{O}_2$  in the system pumped away. The yield is measured by letting the gas expand into the three 5-litre storage flasks (21, on Fig. 13), and reading the pressure on the Hg manometer (31) or Bourdon gauge (29). The conversion of organic matter to and collection of  $\text{CO}_2$  is quantitative. The  $\text{CO}_2$  is then transferred to radon trap 20b through CuO wire trap 25, which is cooled with a dry ice-acetone mixture, to remove traces of water. Then radon trap 20a is cooled with liquid  $\text{N}_2$  and kept at approximately  $-80^\circ\text{C}$  by maintaining the  $\text{CO}_2$  pressure inside at 1 atmosphere. The pressure is maintained by regulating the rate of evaporation of  $\text{CO}_2$  in trap 20b. When all the  $\text{CO}_2$  has evaporated and the pressure has dropped to about 8 mm Hg, the stopcock to the pumps is opened and closed four times. . for 5 seconds each. This pumping removes 95-100 per cent of the radon in the sample, traces of  $\text{O}_2$  and nitrogen oxides, and about 3 per cent of the  $\text{CO}_2$ , depending on the size of the sample. The amount of  $\text{CO}_2$  lost is about  $250\text{ cm}^3$  per sample and depends on the pressure at which pumping is started and on the pumping time, but not on the sample size. From very small samples the radon is removed after the gas is mixed with background gas for counting. Atmospheric oxygen, which condenses in the annulus of trap 20a, causes some trouble with large samples, because with time, sufficient liquid  $\text{O}_2$  accumulates and creates a cold spot inside the annulus. The use of liquid  $\text{O}_2$  instead of  $\text{N}_2$  would eliminate this problem.

Final purification of  $\text{CO}_2$  is achieved by passing the gas over freshly regenerated hot Cu wire in furnace 34 (Fig. 13) at  $420^\circ\text{C}$ . The wire is regenerated between sample preparations using pure  $\text{H}_2$  gas.  $\text{CO}_2$  from soil samples often require several passes over the Cu before an acceptable degree of purity is achieved.

The pure samples are stored in the 5-litre glass flasks (30, on Fig. 13) or transferred to steel cylinders (22).

Every two months a new background and standard gas is prepared for each counter to check on the overall reproducibility of the system and procedures.

#### Release of $\text{CO}_2$ from Shells

Samples composed mainly of carbonates are placed in the shell apparatus 13-19 (Fig. 13) with about 1-litre of distilled water. After removing all the air from the apparatus the sample is dissolved by adding  $\text{H}_3\text{PO}_4$  and the released  $\text{CO}_2$  collected in storage flasks 21. Subsequent steps are as described above for organic samples.

### Counting the Sample

The  $C^{14}$  concentration of samples is measured in one of the proportioned counters described earlier in this report. Experience has shown that the following sequential procedure is satisfactory: background, 2 unknowns, standard, 2 unknowns, background... etc. When a background or standard is to be counted on a weekend the schedule is changed and an unknown is counted instead. Thus a background and standard are counted approximately every 10 days, giving three standard and four background counts (one background is used twice - at the end of one month and at the beginning of the next) for the monthly age calculations.

The background gases are prepared from Precambrian limestone and Pennsylvania anthracite and are counted alternately, as are two separate N.B.S. oxalic-acid standard gas preparations.

Counting periods during the week average 1,200 minutes and on weekends 4,200 minutes. Unknowns are counted once if it is a weekend count, twice if counts are one day, and more often if the statistical analysis of the counting rates, made possible by the Esterline-Angus Operation Event Recorder, reveals greater than random fluctuations.

The 2-litre counter is filled to a pressure of 150 cm Hg at 26°C. Changes in room temperature are corrected for by changing the pressure correspondingly. Samples that are too small to fill the counter to 2 atmospheres are mixed with background gas prior to counting. Mixing is preferred to recalibration of the counter at a lower pressure because it can be done when required without appreciable loss of time or accuracy.

The 5-litre counter is operated mostly at one atmosphere (75 cm). The majority of samples are not big enough for high pressure operation, nor is a need for greater accuracy indicated in most cases. When a number of large old samples of sufficient importance to warrant high pressure operation have accumulated, the counter is calibrated at 4 atmospheres. It has been found that gases giving satisfactory plateaux at a pressure of 1 or 2 atmospheres usually require additional purification when counted at 4 atmospheres. This is due to the increase in the concentration of electronegative impurities with increased pressure.

To check the sample-to-sample purity a pitchblende source is placed near the newly filled counters, the high voltages set near the midway point on the steeply rising portion of the plateau, and the counting rates recorded. Shifts in the operating point, reflecting changes in the concentration of electronegative impurities in the gas, are thus detected within a few minutes. It has been found that an impurity equivalent to a 50 volt shift in the operating point does not affect the sample counting if the high voltage is adjusted properly. Samples stored in the glass filling line rarely require an adjustment of 30 volts or more (perhaps 1 sample in 20), but samples stored

in the Hooke cylinders for 3 to 4 weeks are poisoned by an electronegative impurity apparently given off by the nylon valve seat and/or the compound used by the manufacturer to seal the threaded valve to cylinder joint. This impurity can be removed easily, however, by passing the gas over hot copper wire.

### CALCULATIONS

Age calculations are performed on a monthly basis if no significant shifts in background and standard counting rates are observed during the interval. A close check on the day-to-day performance of the counting equipment is kept with the aid of the previously described pitchblende source test, the alpha discriminators, auxilliary scalers, and Esterline-Angus recorder. Only counts inside the probability range, as predicted from the randomness of radioactive decay, are accepted. For instance, if one of three measurements of the same sample is more than two  $\sigma$  removed from the average, it is rejected. Here  $\sigma$  is the standard deviation of a single measurement and is  $=\sqrt{\text{number of counts/time}}$ . Because most unknowns are counted only twice, the following rule is adopted: a pair of measurements is acceptable if the difference between the pair is less than the sum of the individual standard deviations multiplied by 1.33. This practice should be acceptable because statistics theory permits a total deviation of  $4\sigma$  from the average of 3 measurements. Weekend counts are divided into 10 hour intervals and treated statistically using the 2 out of 3  $\sigma$  criterion before they are accepted.

Since the summer of 1964 all age calculations are carried out by an IBM 1620 computer. The number of counts and counting times of each measurement with the proper sample identification are fed into the computer, which compiles and prints net counting rates, ages, and errors using the equations listed below.

Weighted average counting rates are obtained by the following equations:

$$\begin{aligned} R(I) &= \text{COUNTS (I)} / \text{MINUTES (I)} \\ SQ(I) &= R(I) / \text{MINUTES (I)} \\ W(I) &= 1 / SQ(I) \\ DIV &= \Sigma R(I) W(I) \\ DIVD &= \Sigma W(I) \end{aligned}$$

weighted average counting rate,

$$\text{AVE} = \text{DIV} / \text{DIVD} \tag{1}$$

SIGMA, the standard deviation of the average is calculated as

follows:

$$\begin{aligned} \text{SUMSIG} &= \sum \text{SQ}(I) \\ \text{SUMDEL} &= \sum (\text{AVE} - R(I))^2 \end{aligned}$$

$$\text{If } \text{SUMSIG} < \text{SUMDEL} \begin{cases} N \leq 2, \text{ SIGMA} = \pm \sqrt{\text{SUMDEL}/N} \\ N > 2, \text{ SIGMA} = \pm \sqrt{\text{SUMDEL}/N (N-1)} \end{cases} \quad (2)$$

$$\text{If } \text{SUMSIG} > \text{SUMDEL} \begin{cases} N < 2, \text{ SIGMA} = \pm \sqrt{\text{SUMSIG}/N} \\ N > 2, \text{ SIGMA} = \pm \sqrt{\text{SUMSIG}/N (N-1)} \end{cases}$$

### Legend of Symbols

R	= counting rate of single measurement
(I)	= subscript 1, 2, 3 ... etc. corresponding to the 1st, 2nd, 3rd, ... etc. measurement
SQ	= square of the standard deviation, $\sigma$
$\sigma$	= $\sqrt{\text{COUNTS}/\text{MINUTES}}$
W	= relative weight of single measurement
N	= number of measurements per sample
AVE	= weighted average counting rate
BKGR	= AVE of background
AVEO	= AVE of oxalic-acid standard
AVEU	= AVE of unknown sample
STD	= net average counting rate of standard
SAMPLE	= net average counting rate of unknown sample
SIGMA	= standard deviation of average
SIGMAB	= SIGMA of background
SIGMAO	= SIGMA of oxalic-acid standard
SIGMAU	= SIGMA of unknown sample
SIGSTD	= standard deviation of STD
SIGMAS	= standard deviation of SAMPLE
MR	= mixing ratio = pressure of sample + inactive gas/pressure of sample
LOGF	= natural logarithm
8032.9	= half-life of $C^{14}/\text{LOGF2} = 5568/0.69315$

Since most measurement intervals are of about the same duration the averages are not changed appreciably by omitting the weights from the calculations. It is only when a 3 day weekend count and a 1 day count, or a 20 hour count and an 8 hour count are averaged that weights become significant.

N, the number of single measurements per sample, is seldom more than 2 for unknowns; for background and standard it is generally 4 and 3 respectively, per month.

The choice between SUMSIG and SUMDEL (2) is necessary because either one could be smaller, making SIGMA smaller than is justified by the actual results.

The net standard and sample counting rates and errors are obtained from the following expressions:

$$\begin{aligned} \text{STD} &= 0.95 (\text{AVEO} - \text{BKGR}) \\ \text{SIGSTD} &= \pm \sqrt{(\text{SIGMAO})^2 + (\text{SIGMAB})^2} \end{aligned} \quad (3)$$

$$\begin{aligned} \text{SAMPLE} &= (\text{AVEU} - \text{BKGR}) \cdot \text{MR} \\ \text{SIGMAS} &= \sqrt{(\text{SIGMAU})^2 + (\text{SIGMAB})^2} \cdot \text{MR} \end{aligned} \quad (4)$$

The factor 0.95 in equation 3 is used to bring the  $C^{14}$  activity of the N.B.S. oxalic-acid standard for radiocarbon dating to the same level as that of wood grown in 1850, measured in 1950 and corrected for a 100 year decay of  $C^{14}$ . Thus all ages are quoted with reference to 1950 A.D. For example: a sample with a  $C^{14}$  age of 1,000 years as determined in 1964 using the above standard and correction factor, would actually be 1,014 years old, but is reported as being a 1,000 years old - the age it would have given in 1950.

MR, the mixing ratio, defined in the legend, is greater than one only when a sample has been mixed with inactive gas for counting. By applying MR to the calculation of the error also, SIGMAS is made somewhat larger than it actually would be if a more rigorous calculation were carried out (i.e. figure out AVEU from the number of counts the sample would have produced had there been enough to fill the counter without mixing). This increase in SIGMAS is partly offset by the omission of an error due to mixing (approx.  $\pm 0.2\%$  max.), but still remains on the safe (i.e. large) side.

Finite ages and errors are calculated whenever the net average sample rate, SAMPLE, is equal to or greater than four times the standard deviation SIGMAS, using the following equations:

$$\text{AGE} = 8032.9 \text{ LOGF}(\text{STD}/\text{SAMPLE}) \quad (5)$$

$$\text{ERROR} = \pm \sqrt{\left[ \text{AGE} \right]^2 \left[ \frac{\left( \frac{\text{SIGSTD}}{\text{STD}} \right)^2 + \left( \frac{\text{SIGMAS}}{\text{SAMPLE}} \right)^2}{\left( \text{LOGF} \left( \frac{\text{STD}}{\text{SAMPLE}} \right) \right)^2} + 0.29 \times 10^{-4} \right] + 1.44 \times 10^4 \text{ yr}} \quad (6)$$

If the net sample rate is less than 4 SIGMAS, a greater than age is calculated

$$\text{AGE} > 8032.9 \text{ LOGF (STD (SAMPLE} + 4 \times \text{SIGMAS)) yr (7)}$$

All calculations in this laboratory have been carried out using the value of  $5568 \pm 30$  years for the half-life of  $C^{14}$ , in accordance with the decision of the 5th International Dating Conference at Cambridge in 1962 (Godwin, 1962), and the recommendation of the editors of Radiocarbon. More recent determinations of the  $C^{14}$  half-life by several workers (see references of Godwin, 1962; and Olsson and Karlen, 1963) give an average of  $5730 \pm 40$  years. Conversion of published dates to this basis is accomplished by multiplying them by 1.03.

The last two terms in the error equation take into account errors due to the half-life of  $C^{14}$  and the average variation of  $\pm 1.5\%$  in the  $C^{14}$  concentration of the standard (Willis et al., 1960; this paper). The error term  $1.44 \times 10^4$ , (120 years)<sup>2</sup>, covers the zero age  $C^{14}$  variation in nature. It makes little difference to the resultant error of older samples, but gives a more realistic error for the young samples. For instance, in samples of up to 1,000 years old, this correction generally accounts for about 50 per cent of the age error, in a 10,000 year old sample about 30 per cent, and in a 20,000 year sample about 5 per cent.

No corrections for barometric-pressure fluctuations are applied to the measured counting rates. The observed barometric-pressure fluctuations of  $\pm 1.5$  cm, and barometric-pressure effect of  $-1.2\%$ /cm Hg in the 2 litre counter would, in the worst possible case change the calculated age of samples with counting rates near 4 SIGMAS (i.e. ages of ca 40,000 year) by approximately 4 per cent, and by less than 1 per cent for samples with ages of 30,000 years and younger.

## RESULTS

The large majority of samples measured in this laboratory were of geological interest and have been published in volumes 4, 5, 6, and 7 of Radiocarbon. Papers dealing with specific problems, such as surficial geology of the Canadian Arctic, postglacial uplift, peat bog formation, etc., containing dates produced in this laboratory have been published or are in print (see Fyles, 1963; Craig and Fyles, 1965; Craig, 1964; Blake, 1963; Terasmae and Miryech, 1964; Terasmae and Hughes, 1964; Clarke, 1963; and others).

The results of tests on the performance of counters and equipment are discussed earlier in this paper. What follows is a summary mostly in tabular form, of  $C^{14}$  measurements dealing with interlaboratory checks, sample contamination, and nuclear bomb-produced  $C^{14}$ .

For detailed descriptions of the samples listed in various tables, the reader is referred to published and future volumes of Radiocarbon.

### Results of Check Samples

Before a counter was put into routine operation a number of samples previously dated in other laboratories were run to determine its reliability. Table II lists such samples, together with the comparison dates.

As is evident, satisfactory agreement was achieved in all cases where a finite age was obtained. The extension of the age range using the 5 L counter a 4 atmospheres is shown clearly in Part B of Table II. All Geological Survey of Canada "greater than" dates were calculated using the 4  $\sigma$  criterion. Roughly an additional 5,000 years may be added to the quoted "greater than" ages if the reader is content to use the 95 per cent confidence limit (2  $\sigma$  criterion).

### Contamination in Sea Shells and Peat Samples

$C^{14}$  dates of sea shells have been of considerable interest in the study of chronological events in arctic Canada because of the scarcity of suitable organic materials. However, exchange of carbonate in shells with carbonate in groundwater can lead to contamination of the shell resulting in an erroneous  $C^{14}$  age. To determine the extent of such contamination a number of age measurements were carried out on various shell fractions. The results of these tests are listed in Table III. The second, or innermost fraction is somewhat older in all cases. The first five samples from which the outer 10 per cent had been removed by acid leaching, give an average difference of 1.1 per cent between the two inner fractions, whereas the next seven samples (18-54% leach) give an average difference of 0.5 per cent between the two inner fractions, indicating that leaching does remove contamination. Although the difference between fractions is within statistical limits, chance alone cannot explain the difference because the innermost fraction is older, without exception.

In an attempt to investigate the contention that humic acids of one age can under proper conditions of pH and direction of flow of groundwater contaminate peats of another age, a number of peats were separated into more soluble and less soluble fractions by treating with 2% Na OH followed by HCl and water washes. The results of these tests are listed in Table IV. Some of the samples were filtered using zeolite filter aid, but to make sure that the zeolite did not affect the results an equal amount of zeolite was added to both fractions. Several samples also received an acid preleach prior to the base leach separation. Whatever the treatment, no trend can be observed in the results, suggesting that contamination was absent. This conclusion is



TABLE II

Comparison of Ages of Samples Dated in Various Laboratories

Sample No.	GSC date (yrs)	Comparison date (yrs)	Reference
A. 2L counter at 2 atm.			
GSC - 1	12,400 + 200	12,150 + 250	L-391 D, Lamont V
GSC - 2	7,600 ± 150	7,300 ± 120	S-99, Saskatchewan III
GSC - 4	10,190 ± 120	10,600 ± 320	I (GSC) -185, Isotopes II
GSC - 5	10,140 ± 160	10,220 ± 350	I (GSC) -2, Isotopes I
GSC - 13	29,500 ± 800	29,300 ± 1400	L-424C, Lamont V
GSC - 14	26,000 ± 600	25,900 ± 300	L-221A, Lamont V
GSC - 20	4,280 ± 100	4,600 ± 210	S-25, Saskatchewan II
GSC - 21	10,400 ± 140	10,200 ± 250	S-81, Saskatchewan
GSC - 37	12,600 ± 170	12,800 ± 180	I (GSC)-248, Isotopes II
B. 5L counter at 4 atm.			
		2300	
GSC - 93	36,200 + 500	33,200 + 1800	2L counter, GSC II
GSC - 151	>51,100	>38,200	2L counter, GSC III
GSC - 163	>47,400	>38,800	2L counter, GSC III
GSC - 165	>49,900	>36,000	2L counter, GSC - IV
		+ 2400	
GSC - 202	35,400 + 400	36,500 1900	2L counter, GSC - IV
GSC - 202	35,400 ± 400	35,400 + 2200	L-455B, Lamont VII
GSC - 217	47,700 ± 1200	47,500 ± 250	Gro-2597 (de Vries and Dreimanis, 1960)
GSC - 217	47,700 ± 1200	44,900 ± 1000	Gro-2619 (de Vries and Dreimanis, 1960)
GSC - 237	>54,500	>26,000	L-221C, Lamont III
GSC - 331	>46,600	>35,000	I (GSC)-180, Isotopes II
GSC - 367	>49,000	>38,000	I (GSC)-26, Isotopes I
GSC - 370	>51,100	>38,000	W -157, U.S.G.S. II

TABLE III

Tests for Contamination in Sea Shells

Sample No	Fraction (%)	Age (yr)	Net counting rate (% of standard)
GSC - 61	10 - 50	10,360 + 240	27.50 + 0.39
	51 - 100	10,540 + 210	26.92 + 0.34
GSC - 111	10 - 50	30,300 + 1600	2.30 + 0.23
	51 - 100	36,300 + 2000	1.09 + 0.22
GSC - 119	11 - 70	10,460 + 160	27.18 + 0.25
	71 - 100	10,740 + 170	26.23 + 0.25
GSC - 132	11 - 100	29,430 + 680	2.56 + 0.21
	(1st preparation) 63 - 100 (2nd preparation)	29,800 + 220	2.44 + 0.13
GSC - 146	13 - 55	7,620 + 210	38.72 + 0.44
	56 - 100	8,200 + 220	36.00 + 0.44
-----			
GSC - 207	0 - 20	37,100 + 1400	1.00 + 0.17
	21 - 100	> 37,400	0.28 + 0.17
	21 - 100	> 40,500	0.25 + 0.10
GSC - 212	21 - 53	33,100 + 1200	1.63 + 0.24
	54 - 100	35,900 + 1300	1.14 + 0.18
GSC - 227	18 - 54	11,080 + 160	25.13 + 0.24
	55 - 100	11,300 + 190	24.47 + 0.38
GSC - 243	20 - 100	8,450 + 140	34.88 + 0.27
	(1st preparation) 41 - 100	8,710 + 140	33.80 + 0.23
GSC - 277	23 - 59	> 47,400	0.132 + 0.037
	60 - 100	54,200 + 1800	0.117 + 0.025
GSC - 350	44 - 72	7,860 + 150	37.57 + 0.32
	73 - 100	7,980 + 150	36.97 + 0.29
GSC - 351	49 - 74	5,910 + 140	47.86 + 0.26
	75 - 100	6,010 + 140	47.27 + 0.26

strengthened by the analyses of the untreated portions of GSC-4, -305, and -310, together with the treated portions: no significant differences are observed. However most of the peats are from permafrost regions where movement of groundwater must have been negligible for the duration of the cold periods.

Because the age errors include an error term due to the uncertainty in the zero age activity (see under the section headed Calculations), comparison of age pairs gives better agreement than comparison of per cent counting rates, which do not include errors associated with the standard. However, they are also statistically acceptable.

### Coeval Organic-Inorganic Pairs

Sufficient evidence has been collected by a number of laboratories to show that marine shell ages are reliable and reproducible, providing precautions re contamination are observed. Furthermore, the same reference standard can be used for sea shells and land organic matter. This is so because mixing and atmospheric exchange produce reasonably uniform  $C^{14}$  concentrations throughout the biosphere and surface ocean, and mixing of surface water with  $C^{14}$  deficient deeper water almost exactly compensates for the isotope effect, which tends to concentrate  $C^{14}$  in the surface of the ocean (Craig, 1954). However, Fonselius and Östlund (1959) have found that North Atlantic and Arctic surface water has somewhat lower  $C^{14}$  concentration than water from middle latitudes, suggesting that the ice covering reduces the  $CO_2$  exchange rate between water and atmosphere. Therefore, when more data become available, it may be possible to use a more appropriate standard for arctic shells.

$C^{14}$  ages of coeval fresh-water shells or marl may vary considerably from place to place, depending on the limestone content of the water in which the shells lived (Keith and Anderson, 1963; Rubin and Taylor, 1963). This means that each water body attains its own  $C^{14}$  equilibrium with the atmosphere, depending on the "hardness" of the water. With sufficient experimental data one could eventually set up regional standards, which would permit fairly accurate dating of fresh-water shells. To obtain these data a large number of coeval organic-inorganic pairs, in which the organic specimen obtained its carbon from the atmosphere, would have to be analyzed. A start in this venture has been made in this laboratory and the results are listed in Table V. No general conclusions can be drawn from the few results obtained to date, except that marl or fresh-water shells tend to give greater  $C^{14}$  ages than their organic counterparts. It is interesting to note that the moldy and mold free portions of wood (GSC -216) gave identical  $C^{14}$  ages, suggesting that either the standard sample pretreatment removes contamination caused by molds or that molds live entirely off the carbon of the host.

TABLE IV

Tests for Contamination in Peat Samples

Sample No	Fraction	Age (yr)	Net counting rate (% of standard)
GSC - 4	less soluble	10,050 + 140	28.63 + 0.44
	untreated	10,410 + 150	27.74 + 0.44
GSC - 121	less soluble	10,800 + 100	26.05 + 0.25
	no Na OH leach	10,740 + 180	26.24 + 0.30
GSC - 233	less soluble	7,680 + 140	38.41 + 0.31
	more soluble	7,820 + 140	37.22 + 0.24
GSC - 240	less soluble	10,550 + 160	26.87 + 0.27
	more soluble	10,640 + 150	26.58 + 0.22
GSC - 253	less soluble	6,230 + 150	46.00 + 0.47
	more soluble	6,510 + 150	44.40 + 0.45
GSC - 259	less soluble	>38,800	0.27 + 0.13
	more soluble	>36,400	0.35 + 0.13
GSC - 268	less soluble	>36,000	0.40 + 0.18
	more soluble	>41,200	0.00 + 0.15
GSC - 300	less soluble	2,330 + 150	74.80 + 0.68
	more soluble	2,210 + 130	75.95 + 0.37
GSC - 305	less soluble	220 + 130	97.25 + 0.48
	more soluble	270 + 130	96.73 + 0.42
GSC - 310	untreated	270 + 130	96.70 + 0.37
	less soluble	9,620 + 150	30.18 + 0.23
	more soluble	9,510 + 150	30.61 + 0.23
	untreated	9,620 + 140	30.18 + 0.17

TABLE V  
Comparison of Coeval Organic and Inorganic Materials

Sample No	Fraction	Age (yr)	Net counting rate (% of standard)
GSC - 24	wood	12,200 + 160	21.90 + 0.28
(GSC - 38)	marine shells	12,360 + 140	21.46 + 0.31
GSC - 67	organic residue	12,120 + 140	22.11 + 0.29
	marl carbonate	12,900 + 150	20.07 + 0.20
GSC - 272	peat	6,920 + 140	42.22 + 0.34
	shelly marl	7,600 + 160	38.80 + 0.41
GSC - 216	wood (mold free)	3,660 + 130	63.35 + 0.26
	(moldy)	3,670 + 130	63.73 + 0.32
	fresh water shells	3,650 + 140	63.48 + 0.38
GSC - 266	Whale rib		
	Collagen	8,640 + 140	34.09 + 0.22
	Carbonate	3,260 + 130	66.57 + 0.30
GSC - 355	Whale baleen	1,110 + 130	87.06 + 0.29
GSC - 488	Whale ear (bone)		
	Collagen	980 + 140	88.53 + 0.50
	Carbonate	840 + 130	90.08 + 0.43
GSC - 489	Whale limb		
	Collagen	930 + 130	89.06 + 0.28
	Carbonate	480 + 140	94.14 + 0.58
GSC - 361	Whale vertebra		
	Collagen	3,050 + 130	68.40 + 0.36
	Carbonate	2,310 + 150	75.00 + 0.72
GSC - 362	Whale jaw		
	Collagen	2,820 + 130	70.36 + 0.33
	Carbonate	2,220 + 130	75.80 + 0.33
GSC - 447	Bison jaw		
	Collagen	6,160 + 140	46.48 + 0.27
	Carbonate	1,090 + 140	87.28 + 0.47
GSC - 490	Bison teeth		
	Dentin	6,100 + 180	46.80 + 0.70
	Carbonate	2,130 + 130	76.72 + 0.35
GSC - 449	Charred bone		
	Organic	1,160 + 120	86.50 + 0.29
	Carbonate	390 + 130	95.25 + 0.50
GSC - 450	Whale vertebra		
	Collagen	8,990 + 140	32.66 + 0.20
	Carbonate	4,990 + 140	53.75 + 0.28
GSC - 150	Shells	9,180 + 170	31.90 + 0.13
GSC - 452	Whale bone		
	Collagen	1,380 + 130	84.24 + 0.48
	Carbonate	450 + 130	94.51 + 0.50
GSC - 454	Whale bone (beluga)		
	Collagen	10,420 + 150	27.33 + 0.14
	Carbonate	Modern	105.00 + 0.65
L604A	Shells	10,700 + 200	
L604B	Shells	10,550 + 200	

Bone samples, especially the carbonate in bones, have proven to be unreliable in  $C^{14}$  dating, because the open matrix of the bone permits exchange of bone carbonate with carbonates in the groundwater. To get a measure of the exchange of the carbonates in bone, several bone samples (mostly whale bones) were separated into the inorganic and organic (collagen) fractions using the procedure described by Berger et al (1964). The results are listed in Table V. The carbonate fraction, as expected, is younger, showing that replacement of original carbonate can take place fairly rapidly. However, no significant difference exists between the organic and inorganic fractions of the whale ear bone. This could be due to the fact that the ear bone structure is much more dense and closed than that of the whale limb bone.

The close agreement between the collagen and shells from the location (compare GSC-450 to GSC-150, and GSC-454 to L604A and L604B) provides further evidence that collagen dates are reliable.

Extensive studies on the problem of sample contamination in radio-carbon dating have also been made by Olson (1963).

#### Carbon 14 Concentrations in Douglas Fir and Modern Leaves and Grass

Some of the experimental results shown in Figures 1 and 2 were obtained in this laboratory and are listed in Tables VI and VII for reference. A more detailed discussion of  $C^{14}$  variations in Douglas fir tree rings and possible causes for it is given elsewhere (Dyck, 1966).

The data presented in Table VII are analyses of samples that were collected on or about July 1, at Champlain Lookout (elevation 1040' a.s.l., Long.  $75^{\circ}54'W$ , Lat.  $45^{\circ}30'N$ ), 20 miles from Ottawa. The  $C^{14}$  concentrations of the 1961, 1962, and 1963 growths were determined on untreated samples. The 1964 growth was boiled for half an hour in water prior to combustion. This action was prompted by the repeated haphazard results of previous years, but to no avail. The large observed variations appear to be due to a sampling problem; i.e. one handful of leaves picked from the same tree at the same time as another appears to have a much different  $C^{14}$  concentration. It is possible that the time of year and the stage of growth of the individual leaf are critical. Certainly, the fraction of carbon in the leaf derived from the sap, i.e. the previous year's carbon, must affect the  $C^{14}$  concentration in the leaf appreciably during periods of rapid  $C^{14}$  concentration changes in the atmosphere. The results point out that one cannot pick a batch of leaves at random, do a  $C^{14}$  analysis, and draw refined conclusions from the result.

TABLE VI  
 Variations in the C<sup>14</sup> Concentration of Douglas Fir Tree  
 Rings from Vancouver Island

Growth From - To	Avg. Ring Age A.D.	Avg. Ring Age Before 1960	C-14 Age* Before 1960	% Deviation (D) from standard**
830 - 834	832	1128	1220 ± 80	-17.1 ± 7.2
914 - 934	924	1036	1080 ± 100	-11.1 ± 7.6
1014 - 1034	1024	936	1090 ± 100	-22.4 ± 7.0
1126 - 1136	1131	829	810 ± 90	- 4.6 ± 6.6
1228 - 1238	1233	727	760 ± 60	- 4.3 ± 5.9
1330 - 1340	1335	625	660 ± 60	- 4.5 ± 5.2
1432 - 1442	1437	523	430 ± 50	+10.7 ± 4.9
1524 - 1544	1534	426	260 ± 70	+21.2 ± 5.3
1626 - 1646	1636	324	270 ± 60	+ 5.9 ± 6.3
1728 - 1748	1738	222	110 ± 70	+13.7 ± 5.6
1830 - 1850	1840	120	100 ± 90	+ 2.5 ± 6.3

\*To permit closer inter-comparison of sections, the variations of + 1.5% in the zero age activity of the samples were not included in the calculations of the age errors.

\*\*The % deviation was calculated from the expression

$$D = ((A - A_0)/A_0) 1000$$

where

A = net counting rate of sample

A<sub>0</sub> = 0.95 x net counting rate of N.B.S. oxalic acid standard.

TABLE VII  
 Increase in C<sup>14</sup> Concentration of Leaves and Grass from Champlain Lookout, Ottawa,  
 Expressed in % above Oxalic Acid Standard

Year	Grass	Maple Leaves 2' above ground	Maple Leaves 12' above ground	Elm Leaves 12' above ground	Average
1961*	20.36 ± 0.78	26.36 ± 0.57	23.13 ± 0.68	21.36 ± 0.70	22.80 ± 1.32
1962*	35.42 ± 0.66	31.09 ± 0.84	32.04 ± 0.70	33.12 ± 0.86	32.92 ± 0.93
1963*	68.11 ± 0.98	59.75 ± 0.89	62.89 ± 0.72	67.71 ± 0.74	64.62 ± 2.02
1964*	87.15 ± 1.04	84.61 ± 0.62	83.27 ± 0.76	85.73 ± 1.02	85.20 ± 0.83
1964**	90.08 ± 1.02	84.00 ± 1.15	85.19 ± 1.33	86.95 ± 0.97	86.55 ± 1.27

\*untreated samples

\*\*samples boiled in water prior to combustion



## CONCLUSIONS

The apparatus and procedures described in this paper have yielded reliable radiocarbon dates. Experience gained in making low background detectors indicates that while careful selection of materials is essential, meticulous housekeeping in all phases of the work is of outmost importance. The lowest background was obtained using copper, quartz, and epoxy glue in the construction of the counters. Transistorized electronics and long-life proportional guard tubes also helped to reduce background activity.

Variations in sample pretreatment, in particular sea shells and permafrost peats, have shown that contamination in shells is small and can be reduced further by the removal of as much of the outer layers as possible, whereas the pretreatment of peats appears to be unnecessary.

Purification of CO<sub>2</sub> for operation at 4 atmospheres has proven to be somewhat trying, but the advantage gained in extending the age range has made the extra effort worth while.

## REFERENCES

- Agnew, H.M., Bright, W.C., and Froman, D.  
1947: Distribution of neutron in the atmosphere; Phys. Rev., vol. 72, No. 3, pp. 203-206.
- Berger, R., Horney, A.G., and Libby, W.F.  
1964: Radiocarbon dating of bone and shell from their organic components; Science, vol. 144, pp. 999-1001.
- Blake, Jr., W.  
1963: Notes on glacial geology, northeastern District of Mackenzie, Geol. Surv. Can., Paper 63-28, p. 12.
- Clarke, Jr., A.H.  
1963: Supplementary notes on Pre-Columbian littorina littorea in Nova Scotia; The Nautilus, vol. 77, No. 1, pp. 8-11.
- Craig, B.G.  
1964: Surficial geology of Boothia Peninsula and Somerset, King William, and Prince of Wales Islands, District of Franklin; Geol. Surv. Can., Paper 63-44, p. 10.
- Craig, B.G., and Fyles, J.C.  
1965: Quaternary of Arctic Canada; in Markov, F.C. et al., eds., Antropogene Period in the Arctic and Subarctic; Trans. U.S.S.R. Research Inst. of the Geology of the Arctic, vol. 143, No. S-33 (in Russian with English summary).

Craig, H.

- 1954: Carbon 13 in plants and the relationships between Carbon 13 and Carbon 14 variations in nature; J. Geol., vol. 62, pp. 115-149.

Damon, P.E., Long, A., and Sigalove, F.F.

- 1963: Arizona radiocarbon dates IV; Radiocarbon, vol. 5, pp. 283-301.

Dyck, W.

- 1966: Secular variations in the  $C^{14}$  concentration of Douglas Fir tree rings; Can. J. Earth Sci., vol. 3, pp. 1-7.

Elsasser, W.M., Ney, E.P., and Winckler, F.R.

- 1956: Cosmic ray intensity and geomagnetism; Nature, vol. 178, No. 4544, pp. 1226-1227.

Eriksson, E.

- 1963: Possible fluctuations in the atmospheric  $CO_2$  due to changes in the properties of the sea; J. Geophys. Res., vol. 68, No. 13, pp. 3871-3877.

Fonselius, S., and Östlund, G.

- 1959: Naturally radioactive measurements of surface water from the North Atlantic and Arctic Sea; Tellus, vol. 11, pp. 77-82.

Fyles, J.G.

- 1963: Surficial geology of Victoria and Stefansson Islands, District of Franklin; Geol. Surv. Can., Bull. 101, p. 38.

Godwin, H.

- 1962: Half-life of radiocarbon; Nature, vol. 195, No. 4845, p. 984.

Heymann, D., and Schaffer, O.A.

- 1962: Constancy of cosmic rays in time; Physica, vol. 28, No. 12, pp. 1318-1323.

Kamin, M.D.

- 1963: Early history of Carbon 14; Science, vol. 140, No. 3567, pp. 584-590.

Keith, M.L., and Anderson, G.M.

- 1963: Radiocarbon dating: Fictitious results with mollusc shells; Science, vol. 141, pp. 634-636.

Kulp, L.F.

- 1954: Low level counting, key to advances in radiocarbon dating; Nucleonics, vol. 12, No. 12, pp. 19-21.

- Libby, W.F.  
1955: Radiocarbon dating; 2nd edition, The University of Chicago Press.
- McCallum, K.F., and Wittenberg, F.  
1962: The University of Saskatchewan radiocarbon dates III; Radiocarbon, vol. 4, pp. 71-80.
- Olson, E.A.  
1963: The problem of sample contamination in radiocarbon dating; Ph.D. Thesis, Columbia University.
- Olson, I.V., and Karlen, I.  
1963: The half-life of  $C^{14}$  and the problems which are encountered in absolute measurements on Beta-decaying gases; Radioactive Dating, International Atomic Energy Agency, Vienna.
- Radiocarbon  
Published annually by The American Journal of Science, Yale University, New Haven, Connecticut.
- Rubin, M., and Taylor, D.W.  
1963: Radiocarbon activity of shells from living clams and snails; Science, vol. 141, p. 637.
- Rumbaugh, L.H., and Locher, G.L.  
1936: Neutrons and other heavy particles in cosmic radiation of the stratosphere; Phys. Rev., vol. 49, p. 855.
- Starik, I.Y., Arslanov, Kh. A., and Zharkov, A.P.  
1961: Scintillation technique for counting natural radiocarbon and its use for determination of absolute age; Soviet Radiochemistry (Radiokhimiya), vol. 2, No. 182, pp. 67-68.
- Starik, I.E., Arslanov, Kh., and Klener, I.R.  
1963: Improved procedure for chemical preparation of samples for radiocarbon dating by the scintillation method; Soviet Radiochemistry, vol. 5, No. 2, pp. 174-179. (English translation of radiokhimiya).
- Suess, H.E.  
1960: Secular changes in the concentration of atmospheric radiocarbon; Nuclear Science Series Report Number 33, National Academy of Sciences, National Research Council, Publication 845, pp. 90-94.
- Tamers, M.A., Stipp, F.F., and Collier, F.  
1961: High sensitivity detection of naturally occurring radiocarbon - I; Geochem. et Cosmochem. Acta., vol. 24, No. 3/4, pp. 266-276.

Terasmae, J., and Miryneck, E.

- 1964: Postglacial chronology and the origin of deep lake basins in Prince Edward county, Ontario; Publication No. 11, Great Lakes Research Division, The University of Michigan, pp. 161-169.

Terasmae, J., and Hughes, O.L.

- 1964: Late-Wisconsinan chronology and history of vegetation in the Ogilvie Mountains, Yukon Territory, Canada; Proceedings XXII International Geological Congress, India 1964 (in print).

Thellier, E., and Thellier, O.

- 1959: Sur l'intensite du champ magnetique terrestre dans le passe historique et geologique; Annales de Geophysique, tome. 15, No. 3, pp. 285-376.

Vries, de. H.

- 1957: The removal of radon from CO<sub>2</sub> for use in C<sup>14</sup> age measurements; Appl. Sci. Res., vol. 6, Section B, pp. 461-470.

- 1958: Variation in concentration of radiocarbon with time and location on earth; Koninkl. Nederlandse Akad. Wetensch. Proc., Sec. B, vol. 61, No. 2, pp. 1-9.

Vries, de. H., and Dreimanis, A.

- 1960: Finite radiocarbon dates of the Port Talbot Interstadial deposits in southern Ontario; Science, vol. 131, pp. 1738-1739.

Willis, E.H., Tauber, H., and Münnich, K.O.

- 1960: Variations in the atmospheric radiocarbon over the past 1300 years; Am. J. Sci., Radiocarbon Supplement, vol. 2, pp. 1-4.