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THE GEOLOGICAL SURVEY OF CANADA
RADIOCARBON DATING LABORATORY

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Canada

1985

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CONTENTS

* Although SI units are used throughout the text, the dimensions for the counters are quoted as actual measurements and not metric equivalents because the counters are fabricated from materials that are still sold/provided/available in 'Imperial Measure'.

THE GEOLOGICAL SURVEY OF CANADA RADIOCARBON DATING LABORATORY

Abstract

The Radiocarbon Dating Laboratory of the Geological Survey of Canada began routine ^{14}C age determinations in 1961 using a 2 litre copper, proportional counter and CO_2 as the counting gas. This counter is operated routinely at a pressure of 2 atmospheres where the maximum dating limit is approximately 40 000 years using the 4σ criterion.

In 1964 a 5 litre counter was put into operation. Routinely this counter is operated at a pressure of 1 atmosphere where its dating limit is approximately 40 000 years. When operated at 4 atmospheres its age limit increases to about 54 000 years.

Organic samples are burned in a stream of oxygen and the CO_2 released is purified on passage through a series of chemicals and traps. Inorganic samples are dissolved in phosphoric acid.

Up to the end of 1983 more than 3700 age determinations have been carried out on various types of sample material. Since 1963 twenty-three Geological Survey of Canada Date Lists have been published.

The Laboratory also carries out a program of ^{14}C 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 ^{14}C distribution and circulation in nature.

Résumé

Le Laboratoire de datation de la Commission géologique du Canada a commencé à faire des déterminations au ^{14}C en 1961, au moyen d'un compteur proportionnel en cuivre de 2 litres rempli de CO_2. Ce compteur est habituellement maintenu à une pression de 2 atmosphères, sa limite maximale de datation étant d'approximativement 40 000 années au moyen du critère 4σ.

Le Laboratoire a fait l'acquisition d'un compteur de 5 litres en 1964. La pression courante est de 1 atmosphère. On peut confirmer des âges atteignant à peu près 40 000 ans. Lorsque cette pression est portée à 4 atmosphères, il est possible de dater des échantillons de 54 000 ans.

Les matières organiques à dater sont brûlées au moyen d'un jet d'oxygène pur. Le CO_2 ainsi libéré est épuré en le faisant passer dans une série de produits chimiques et de circuits. La matière inorganique, par contre, est dissoute dans de l'acide phosphorique.

À la fin de 1983, le Laboratoire comptait à son actif 3 700 datations de divers types d'échantillons. De plus, depuis 1963, la Commission géologique a publié vingt-trois listes de dates.

Le Laboratoire effectue ainsi des datations par le ^{14}C d'échantillons dont on connaît déjà l'âge afin de confirmer la précision de la méthode et d'en apprendre plus sur la répartition et la migration dans la nature du ^{14}C naturel et synthétique.

INTRODUCTION

The radiocarbon method of dating was developed by the late W.F. Libby (1955) at the University of Chicago in the late 1940s.

The term "radiocarbon" refers to the naturally occurring radioisotope of carbon, ^{14}C, which has an atomic weight of 14 mass units and a half-life of 5730 years (Godwin, 1962). Naturally occurring ^{14}C is produced only by the indirect reaction of cosmic radiation from outer space with the Earth's upper atmosphere above an altitude of approximately 10 000 m. Cosmic rays, consisting mainly of protons and travelling at very high velocities, enter the atmosphere and collide with the nuclei of the atoms making up the atmospheric gases. These collisions produce neutrons.

Radiocarbon is produced by the interaction of these neutrons (η) with the nitrogen in the upper atmosphere and follows the reaction:

$$^{14}N + \eta \rightarrow {^{14}C} + {^1H}$$

The ^{14}C atoms produced are oxidized to radioactive carbon dioxide ($^{14}CO_2$) by atmospheric oxygen and this $^{14}CO_2$ mixes with the ordinary CO_2 of the atmosphere and thus takes part in the normal life-cycle of CO_2. Plants absorb the CO_2 from the air through the process of photosynthesis, animals eat the plants, CO_2 exchange between the atmosphere and the oceans and other water bodies provides a continuous supply of ^{14}C 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 ^{14}C concentration of the medium from which they draw their carbon. When an organism dies, carbon uptake stops but the incorporated ^{14}C continues to decay at a fixed rate determined only by its decay constant. The amount of ^{14}C in a specimen can be measured in the laboratory, and by combining this with the ^{14}C concentration in the specimen when it was living together with the decay constant of ^{14}C, the time elapsed since the organism died (radiocarbon age) can be calculated. The live (or Zero) age ^{14}C concentration is determined by measuring the natural ^{14}C concentration of a living organism (or organic standard) and assuming that the unknown organism had the same ^{14}C concentration when it was alive.

Hence the radiocarbon dating method is based essentially on the assumption that there has been a constant rate of production and distribution of ^{14}C in the various exchangeable carbon reservoirs (atmosphere, oceans and other water bodies, and living or decaying organic matter) of the earth for thousands of years. If this assumption is correct then there exists at the present time a complete balance between the rate of disintegration of radiocarbon atoms and the rate of assimilation of new radiocarbon atoms for all material in the life cycle. For example, a tree, or any other living organism, is in a state of equilibrium between the cosmic radiation and the natural rate of disintegration of radiocarbon so long as it is alive. Refinements in ^{14}C measurement techniques in recent years have shown deviations from the constant ^{14}C distribution and production assumption; however, these deviations are not serious enough to invalidate the dating method.

Two man-made phenomena affecting the natural ^{14}C concentration in the atmosphere are worth mentioning. The first is known as the "Suess" (named after its discoverer) or "industrial" effect which results in the dilution of the ^{14}C concentration in the atmosphere and is caused by the great amount of "dead" CO_2 (i.e. CO_2 not containing ^{14}C) which has been produced by the combustion of fossil fuels (coal and petroleum) since the start of the industrial era. It has been estimated that the activity of atmospheric CO_2 decreased by about 2% to 3% during the period 1850-1950. This dilution is still continuing. The result of this industrial effect is to make samples that died during this time period appear slightly older than their true age.

The second man-made phenomenon is a result of the testing of nuclear weapons. When these weapons are exploded in the upper atmosphere, the neutrons formed produce radiocarbon atoms which are then introduced into the dynamic carbon reservoir as $^{14}CO_2$. During the peak period of testing in 1963-1964, radiocarbon concentrations approximately 90% above normal were reported in the Northern Hemisphere (Lowdon and Dyck, 1974). The concentration in 1983 had decreased to about 30% above pre-bomb times and has continued to decline.

In summary, the radiocarbon age determination method is based upon the fact that ^{14}C is radioactive and hence decays. On decaying, the ^{14}C reverts to ^{14}N with the emission of a β-particle (electron). The rate of decay of ^{14}C is quoted in terms of its half-life, which is the time it takes for one half of any given quantity to disintegrate. Libby (1955) determined the half-life to be 5568 ± 30 years. More recent determinations have set the half-life at 5730 ± 40 years. For convenience and by convention, however, ^{14}C dates are continued to be reported and published using the 5568-year value unless otherwise stated in publications.

Since the original work by Libby, more than 100 radiocarbon dating laboratories have been set up throughout the world. While the first laboratories counted the emanations from pure, solid carbon, all laboratories today convert the samples into either a gas (carbon dioxide, methane, acetylene, or ethane) or into a liquid (benzene) for counting purposes. At the present, CO_2 gas counting is still the most widely used method in radiocarbon dating laboratories, followed closely by liquid scintillation counting of benzene.

HISTORICAL DEVELOPMENT OF THE RADIOCARBON DATING LABORATORY

Active development of the Geological Survey of Canada Radiocarbon Dating Laboratory began late in 1959. Routine age determinations began early in 1961 using a 2 litre (2 L) copper, proportional counter and CO_2 as the counting gas. In 1964 a 5 litre (5 L) counter was put into operation which, when operated at 4 atmospheres, extended the age limit to about 54 000 years, compared to 40 000 years for the 2 L counter at 2 atmospheres and the 5 L counter at 1 atmosphere. A 1 litre (1 L) counter was fabricated and put into operation in June 1970. Because of the larger age error associated with this counter, however, it has never been used in a routine manner.

Up to the end of 1983, more than 3700 age determinations have been carried out on various types of sample material. Since 1963 twenty-three Geological Survey of Canada Radiocarbon Date Lists have been published. Lists I to XI were published first in the journal *Radiocarbon* and then reprinted as Geological Survey of Canada papers. Lists XII to XXIII were published as Geological Survey of Canada papers only.

The laboratory has also continuously carried out a program of ^{14}C 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 ^{14}C distribution and circulation in nature.

In 1969 the decision was made to submit all samples with a radiocarbon age of less than 5000 years for $^{13}C/^{12}C$ determinations in order to evaluate, and correct for, the effects of carbon isotope fractionation. The 5000 year

"cut-off" point, however, was arbitrary. Since 1971 the decision to obtain $^{13}C/^{12}C$ ratios has been based on need, rather than age of sample.

This report is an updated version of a report by Dyck (1967) and will serve to highlight important changes that have occurred in laboratory procedures and apparatus since 1966.

APPARATUS

Sample Counters

Because of the low levels of radiocarbon existing in nature (natural atmospheric abundance of approximately $10^{-10}\%$), extremely sensitive measuring techniques must be used for its detection. It is also essential, however, that the procedure must be as simple and as reliable and reproducible as possible. The simplest method is to use the material in the gaseous state as carbon dioxide in which the sample being measured constitutes part of the gas phase of the detecting instrument. It is then best to use a proportional type counter operating at as high a pressure of gas as is feasible.

Essentially, a counter consists of a cylinder (commonly copper), vacuum sealed at both ends, with a wire along its axis. This centre wire acts as the anode. Simply, when a voltage of a predetermined magnitude is applied to the central wire (anode), the gas in the counter is ionized and the decay products of the radioactive carbon (β-particles) are collected on the anode, amplified electronically, and measured.

At present the Radiocarbon Laboratory of the Geological Survey of Canada has three copper proportional counters of volumes 1, 2, and 5 L. The 2 L counter is routinely operated at 2 atmospheres pressure, and the 1 L and 5 L counters at 1 atmosphere. On occasion the 5 L counter is operated at high pressure (4 atmospheres). This extends the workable age limit to about 54 000 years as compared to about 40 000 for the 2 L counter at 2 atmospheres and the 5 L counter at 1 atmosphere, and 25 000 years for the 1 L counter at 1 atmosphere.

2 Litre Counter

During the 24 years in which the laboratory has been in operation, three identically designed 2 L counters have been used. The original one was put into operation in 1961 and ran routinely until the spring of 1971 when, for still unexplained reasons, it failed to function properly and was discarded. A second 2 L counter was put into operation in August 1971. This counter broke down in December 1974 when air-conditioning problems in the counting laboratory created high humidity levels. A third counter was put into operation in April 1975 and has been routinely operated since that time.

A cross-sectional drawing of the "service end" of the 2 L counter is shown in Figure 1. The inside wall of the counter was cleaned by machining away a 30 mil layer and rinsing with distilled water and acetone prior to assembly. Assembly was completed as soon as possible after machining in order to avoid undue exposure of the surfaces to airborne radioactive particles. The copper end plates and quartz

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

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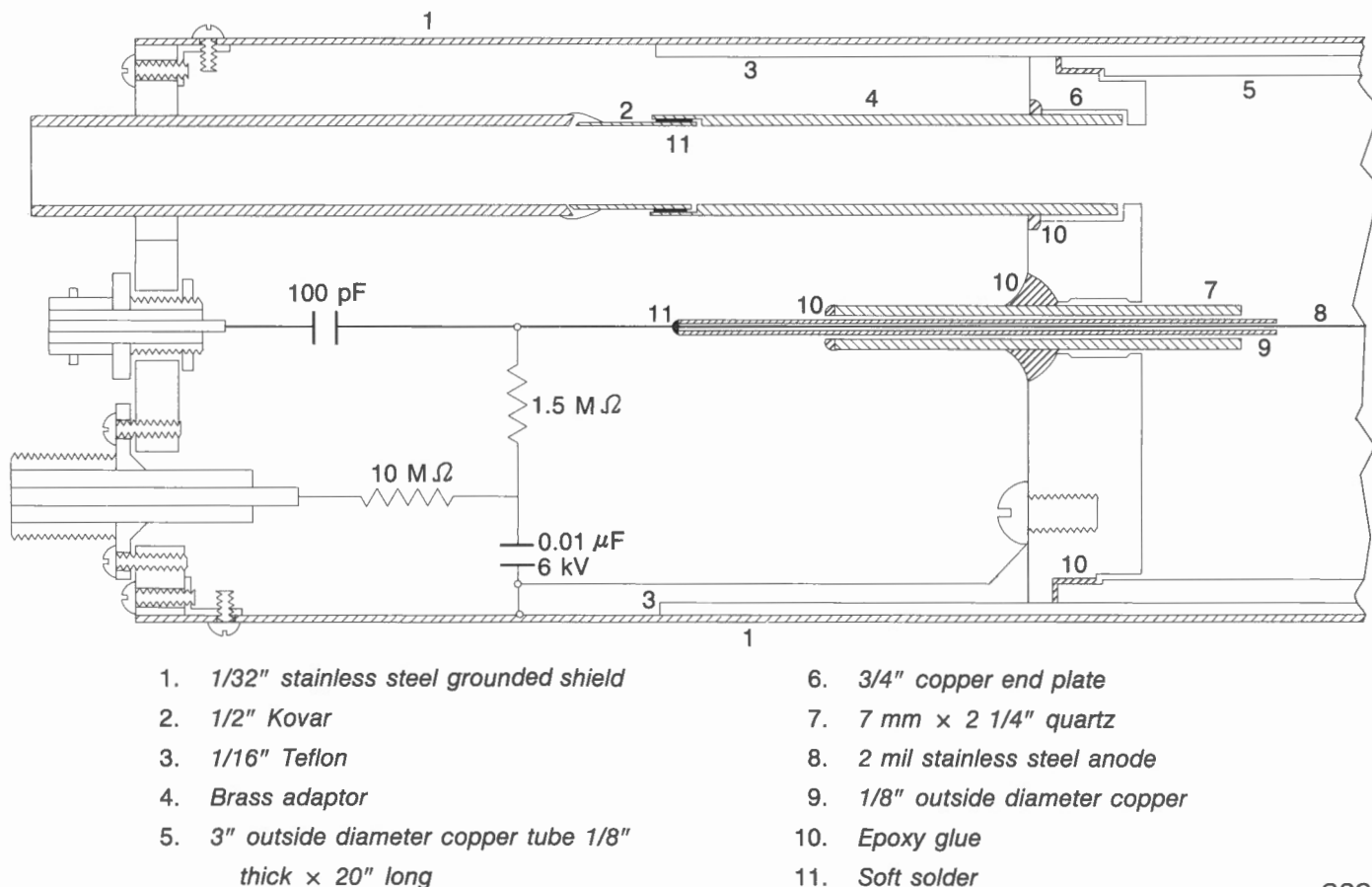**Figure 1.**   Cross-section of the "service end" of the 2 L counter.

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 permits safe operation of the counter cathode at potentials other than ground.

The 2 L counter is operated routinely at a pressure of 2 atmospheres where the maximum dating limit is approximately 40 000 years using the 4 sigma criterion.

5 Litre Counter

After considerable testing and modification, a 5 L counter, designed to operate at pressures of up to 5 atmospheres, was put into operation in 1964. This counter is still being used routinely at the present time. A cross-sectional view is shown in Figure 2. This counter was constructed from a 5 $1/8$ inch outside diameter, $1/8$ inch wall copper tube having an overall length of 20 inches. Procedures and precautions similar to those for the 2 L counter were used in the cleaning and assembly. There are two important differences in the assembly of these counters. Firstly, the end plates of the 5 L counter were welded in place rather than glued. This reduced the amount of epoxy glue exposed to the counting chamber and also strengthened the ends sufficiently to allow the counter to be operated at high pressure (4 atmospheres). Secondly, the sealing washer in the front-end insulator was made from 16th Century lead because of its low radioactive lead content. Routinely this counter is operated at a pressure of 1 atmosphere where its dating limit is approximately 40 000 years (4 sigma criterion). Occasionally, however, it is operated at 4 atmospheres when its age limit increases to about 54 000 years.

1 Litre Counter

A 1 L counter with an acceptably low background was fabricated and put into operation in 1970. The basic design and assembly of this counter is the same as for the 2 L counter described above. A copper tube, 2 $1/8$ inches outside diameter, with an $1/8$ inch wall and 18$1/4$ inches long, was used for construction. This counter has never been used on a routine basis because of its limited age range (modern to approximately 25 000 years at 1 atmosphere) and its associated higher age error.

The more significant performance characteristics of these three counters have previously been published and have not changed significantly over the years (Dyck, 1967; Lowdon et al., 1971).

Counter Shield

The construction of the detecting instrument (counter) must be such as to ensure the maximum difference between the count rate of a sample and the count rate of the background. All ^{14}C laboratories have a "built-in" background count, which comes from neutrons produced by cosmic radiation and gamma radiation emanating from brick walls, concrete floors, etc. This background must be cut down as low as possible by building some type of shield around the counters. The Geological Survey of Canada counting laboratory is located in the subbasement of an eight storey building, thus taking advantage of the natural shielding against cosmic rays offered by the building. The room is air-conditioned and an electrostatic air cleaner prevents the accumulation of long-lived radioactivity in the room. The counter shield is shown in cross-section in Figure 3.

1. Copper end plate	4. Copper anode guide	7. Araldite
2. Quartz insulator	5. Gas port	8. Soft solder
3. 2 mil stainless steel anode	6. Old lead washer	9. Weld

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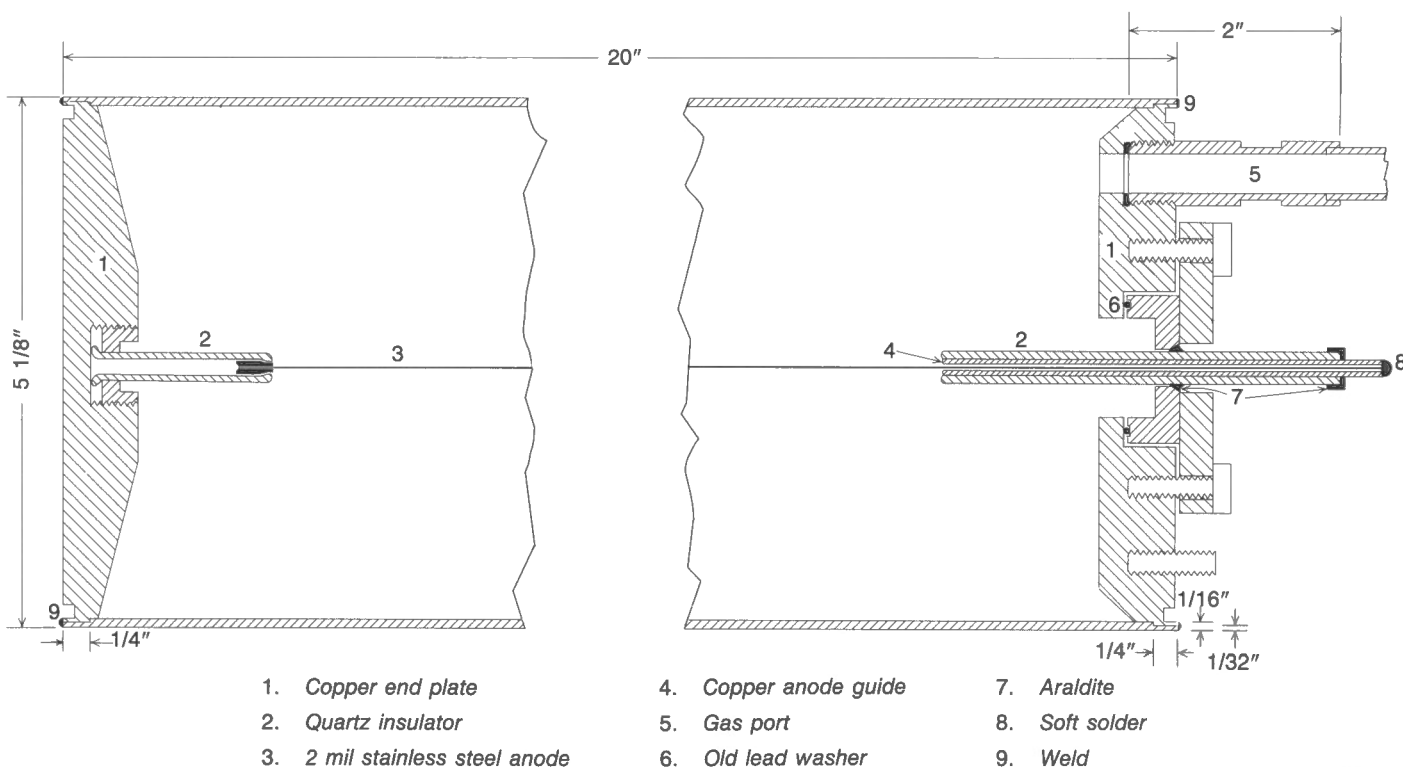
Figure 2. Cross-section of the 5 L counter.

40"

1

2

8"

$\frac{1}{2}$"

4"

8" 4" 15$\frac{1}{2}$" 4" 8"

3 4 5 6

14"

8

7

6"

10 9

41$\frac{1}{2}$"

$\frac{1}{2}$" 2"

4"

6" 6

8"

24"   concrete pedestal
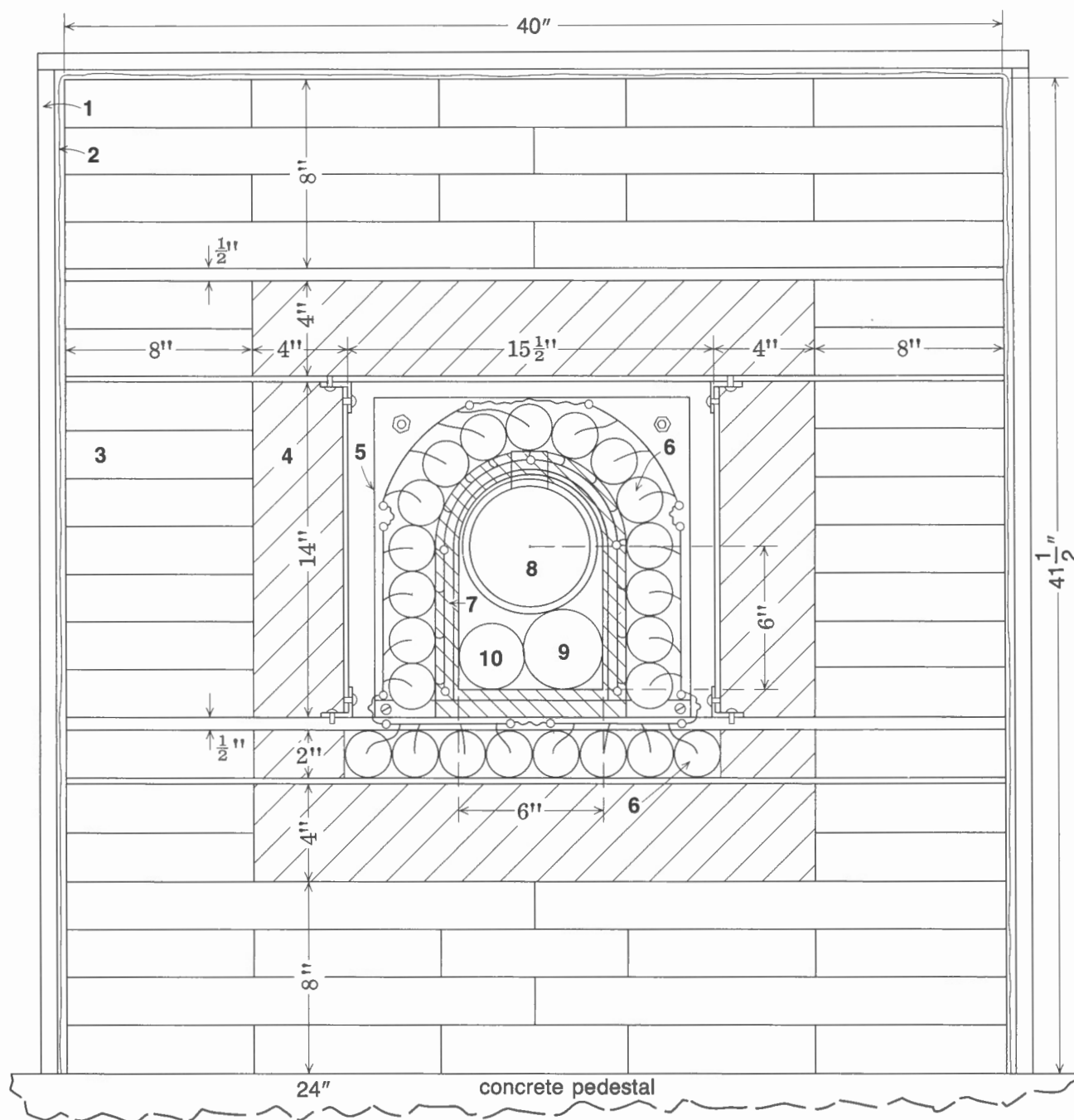
1. 3/4" plywood
2. Polyethylene sheet
3. Cast iron
4. Paraffin
5. Plastic guard counter support

6. Guard counters
7. Hg vessel, 1" × 36" stainless steel
8. 5 L counter
9. 2 L counter
10. 1 L counter

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

5

Eight inches of cast iron, 4 inches of paraffin, 23 cosmic-ray guard tubes, and 1 inch of mercury constitute the shield. The shield is approximately 60 inches long. In order to prevent the accumulation of dust inside the shield by thermal convection currents, the whole assembly is wrapped in polyethylene sheet and covered with plywood. Provision is made for access through openings at the front of this structure, which is referred to as the "castle" (Fig. 3, 4).

The cast iron layers of bricks shield the counters against gamma radiations emanating from brick walls and concrete floors. The paraffin layer is placed inside the iron in order to slow down and absorb neutrons produced by cosmic rays in the atmosphere, building, and iron shield. The space inside the iron-paraffin assembly provides enough room for 4 preamplifiers, a stainless steel vessel containing mercury, a ring of 23 cosmic ray tubes, and 3 counters of 5 L, 2 L, and 1 L capacities (Fig. 4). The mercury vessel is constructed from 30 mil stainless steel and provides a 1 inch thick by 36 inches long layer of mercury as an additional gamma-ray shield for the counters. The 23 cosmic ray counters are positioned as shown in Figures 3 and 4 and constitute what is commonly called the "guard". The guard tubes make up part of what is termed the anticoincidence circuit. This device is used to eliminate any cosmic radiation that passes through the outer shielding. When a passing cosmic ray activates a guard tube and also activates the sample counter, the anticoincidence circuit comes into play and the count is automatically eliminated from the record.
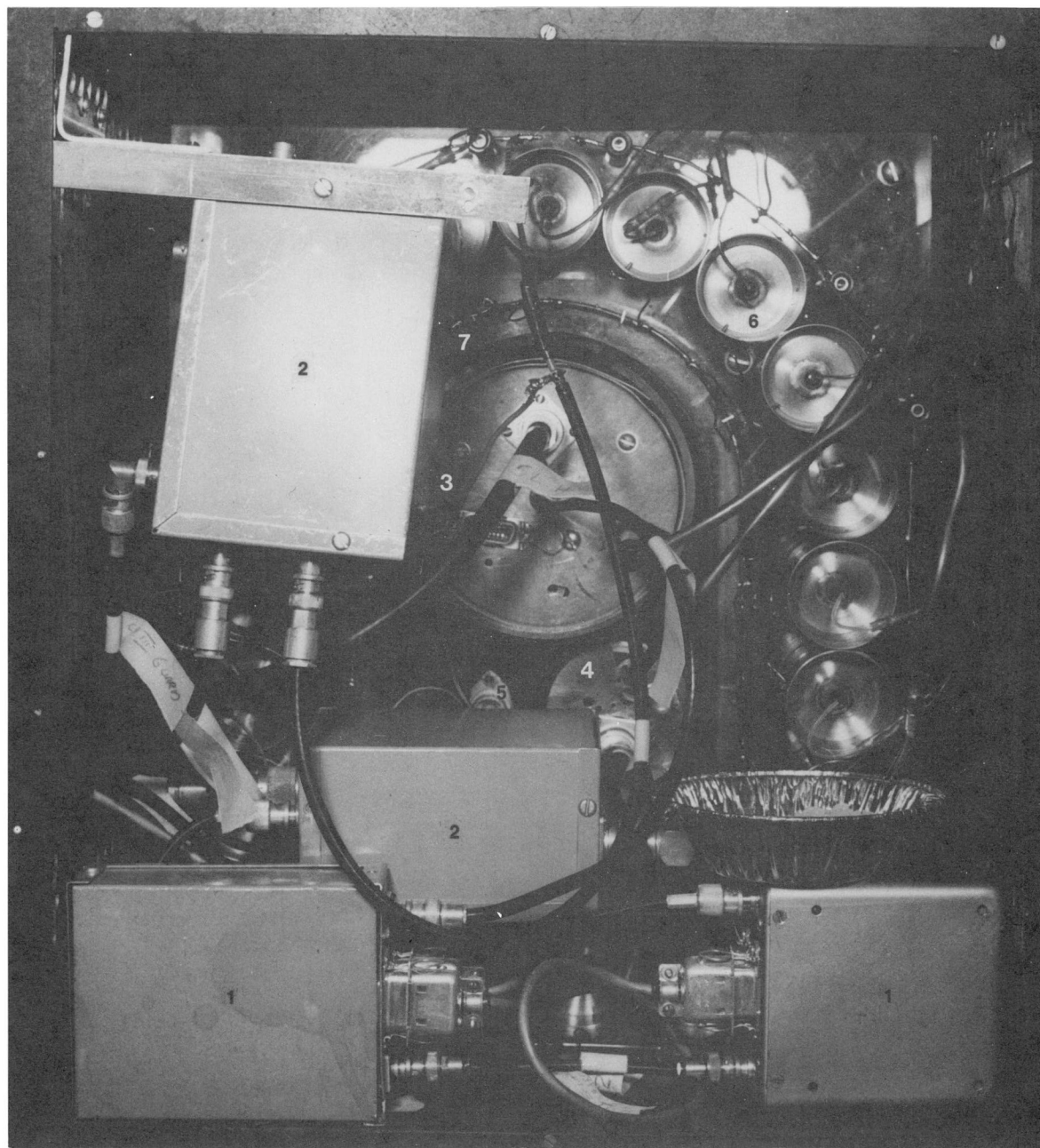
1.	Preamplifiers	3.	5 L counter	5.	1 L counter	7.	Mercury shield
2.	Discriminators	4.	2 L counter	6.	Guard tubes		

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Figure 4.   Inside the "castle".

Electronic Equipment

The basic electronic equipment consists of a transistorized Sharp low-beta unit, various Canberra scalers for totalizing counts, Fluke high voltage supplies, and a ten pen Esterline-Angus event recorder. The latter provides a permanent and continuous record of the output of the various scalers. The basic electronic units are shown in Figures 5 and 6. Positioning of the preamplifiers and discriminators inside the "castle" is shown in Figure 4. A typical recording of the counting rates is given in Figure 7. Signals from selected decade scaler outputs are fed into univibrator type circuits which activate the relay-driver pen mechanisms of the recorder. The recording consists of blips made by the pens on the chart which move at a constant, known speed. Each blip represents 10^n counts where $n = 1,2,3$, etc. corresponding to the 1st, 2nd, 3rd, etc. decade output which is selected as desired, depending on the counting rate of the particular channel. Thus, large counting rate fluctuations, power failures, electronic breakdowns may be detected more readily. The recorder has been most useful in determining the reliability (statistical variation) of weekend counts, thus eliminating the need for a second count for samples counted

Guard	23 proportional counting tubes	MA	Main amplifier
5 L	5 L sample counter	NP	Noise pick up
2 L	2 L sample counter	UV	Univibrator
PA	Preamplifier	AC	Anticoincidence circuit
D	Discriminator		
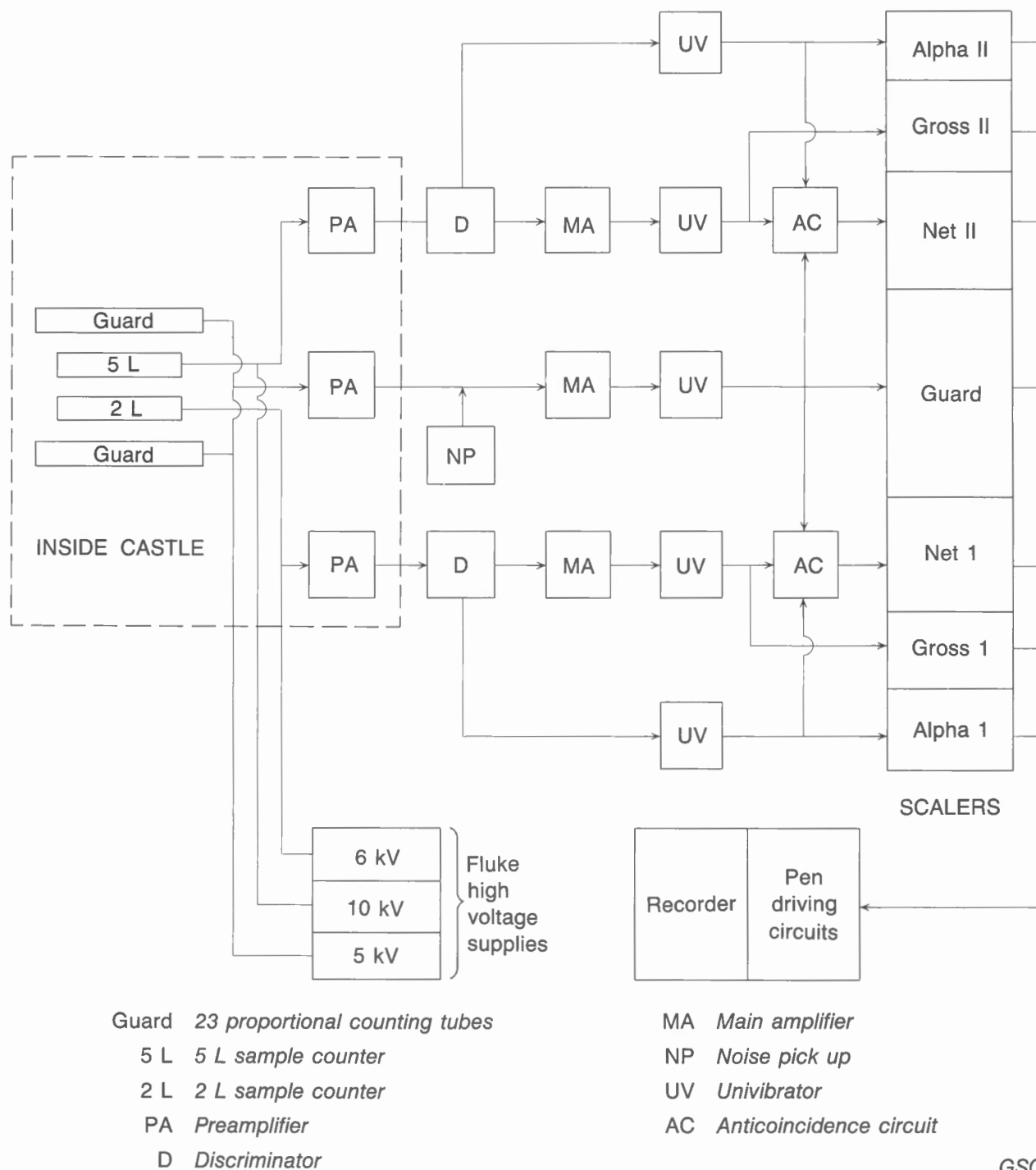
Figure 5. Flow diagram of the electronics.

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7
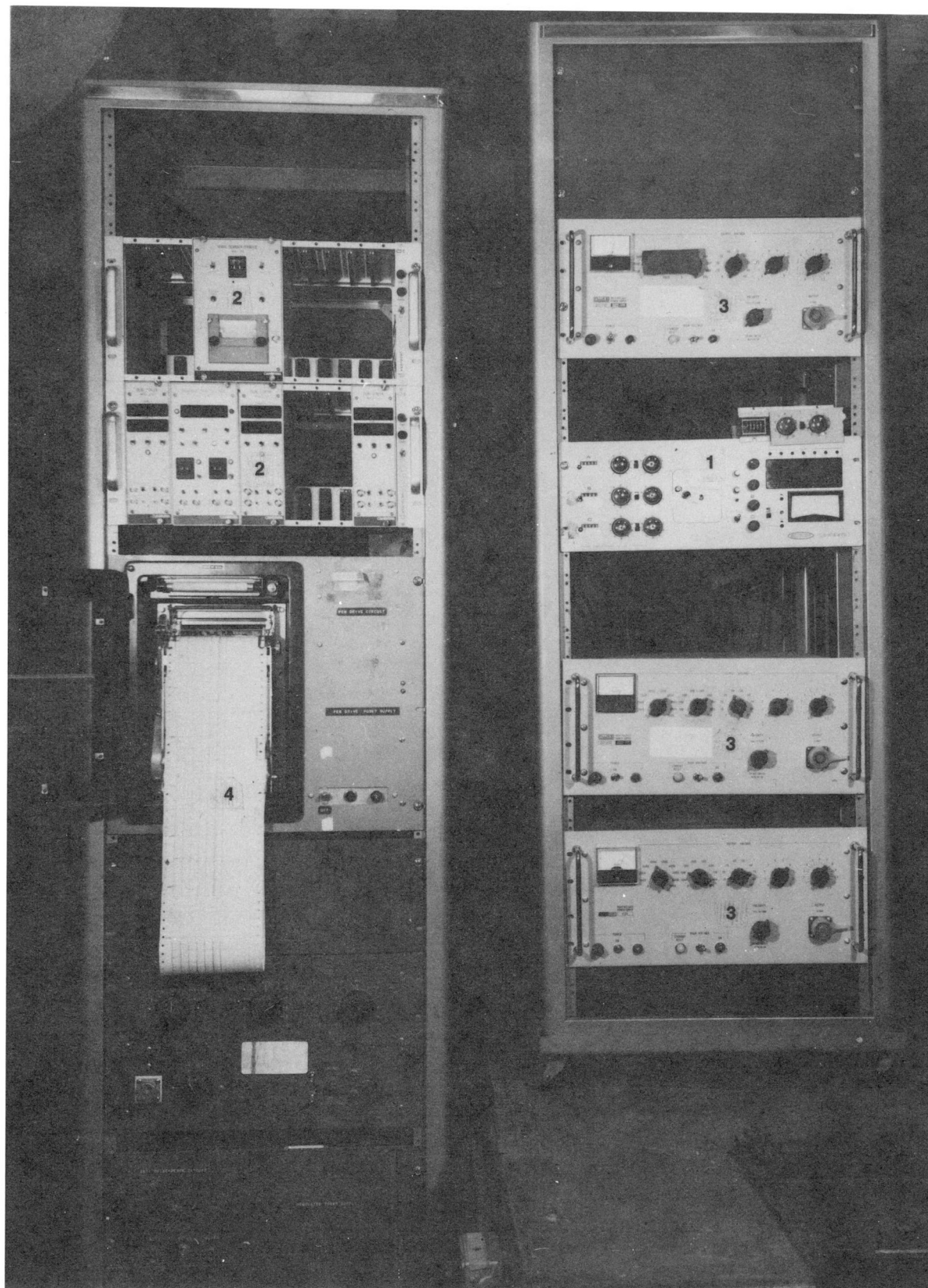
1. Sharp low-Beta unit   3. Fluke high voltage supplies

2. Canberra scalers   4. Esterline-Angus recorder

Figure 6. *Electronic equipment.*

over a weekend. The counts recorded by pens 1 to 7 (from left to right in Fig. 6, 7) represent the guard, 2 L gross, 2 L net (sample count plus background count), 2 L alpha, 5 L gross, 5 L net, and 5 L alpha counting rates, respectively.

Sample Preparation and Purification System

The original method used in the laboratory for the preparation and purification of CO_2 gas from organic samples has been fully described by Dyck (1967). Minor changes were made in this method throughout the years (Lowdon and Blake, 1968, 1970; Lowdon et al., 1969. However, problems were continuously encountered in the preparation and purification of CO_2 from bone samples. On occasion,

the quartz combustion tube exploded, possibly as a result of the formation of phosgene gas. Also, occasionally, it was impossible to purify the gas sufficiently to obtain acceptable counting characteristics. These excess impurities were likely due, in most part, to the presence of nitrogen compounds which were not readily removed in the original purification system. In 1971 an attempt was made to establish a separate gas preparation and purification technique for bone samples. This method ($SrCO_3$) has been described previously (Lowdon et al., 1971). Although this new technique appeared to satisfy all requirements such as acceptable reproducibility of results and absence of carbon isotope fractionation (Table 1), it was not adopted as a routine method for bone samples mainly because of the time involved in preparing the

Figure 7. Esterline-Angus chart recording.

Table 1. Comparison of results obtained by different preparation techniques of bone samples

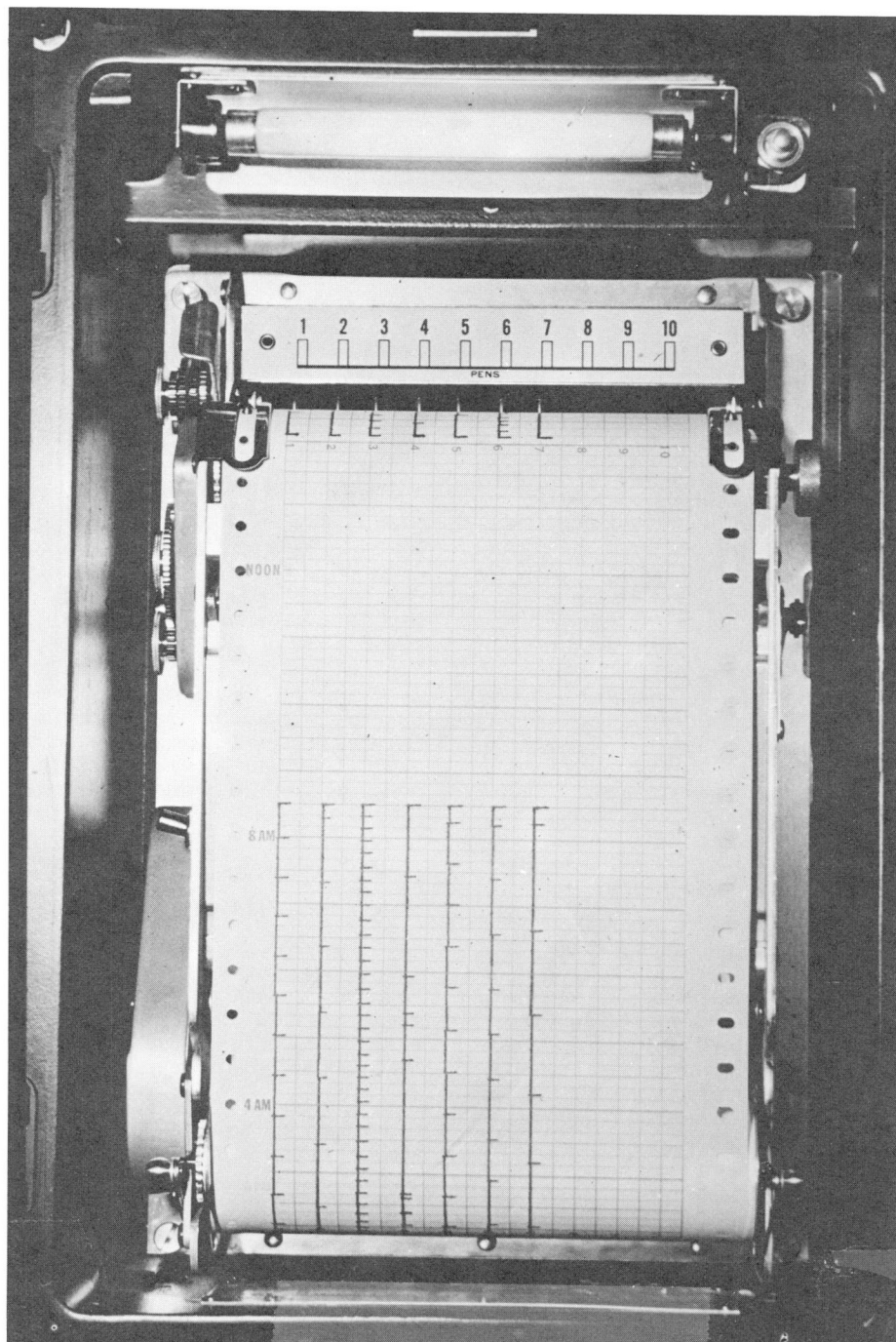| Sample Number	Preparation Technique*	Uncorrected Age (BP)	$\delta^{13}C$ ($^o/_{oo}$)	Corrected Age (BP)
GSC-1219	Old	2 260 ± 130	-21.2	2 320 ± 130
GSC-1219-2	New	2 210 ± 130	-21.2	2 270 ± 130
GSC-1220	Old	31 900 ± 630	-18.7	32 000 ± 630
GSC-1220-2	New	31 600 ± 690	-19.8	31 700 ± 630

* "Old" refers to the preparation technique used in the laboratory prior to October 1976. "New" is the $SrCO_3$ technique used now and described in this report.

gas for counting. During 1976 a further concerted effort was made to try and solve the bone problem. The resulting new method of gas preparation and purification described below is now routinely used for all organic samples (Lowdon et al., 1977).

A schematic flow diagram of the new system is shown in Figure 8. Although the legend describes most of the components adequately, a few points of clarification are required. In the "Organic Combustion System" (Fig. 8) the Drierite and Ascarite in Trap 2 are used to remove any traces of water and CO_2, respectively, which might be present in the cylinder of commercial oxygen. Trap 3, containing sulphuric acid, removes any additional water and also serves to give a rough indication of the oxygen flow rate. The empty 2000 mL flask is used as a precaution to prevent any acid from entering the sample combustion tube (4). The combustion tube is made of clear quartz tubing (approximately 32 mm O.D., 2 mm thick, and 120 cm long) with removable rubber stoppers and ceramic heat reflectors at each end. A stainless steel tube (approximately 29 mm O.D. and 30 cm long), cut in half along its length, is used as a sample "combustion boat" (5). Trap 8 is used to remove water formed during the combustion of the sample. The glass wool in the absorption bottle (9) removes any particulate copper oxide carried out of the furnace in the gas stream. Any halides in the gas stream are precipitated by the silver nitrate in bubbling tube 10 and incompletely reacted sulphur and nitrogen compounds are oxidized by the chromic acid in bubblers 11 and 12. Trap 13, referred to later as a bubbling column, is 800 mm in height and 31 mm I.D. The fritted glass bubbler ensures a good dispersion of the gas as it flows up the bubbling column. All connections between 1 and 13 in Figure 8 are made with high quality rubber tubing. This section of the system is therefore operated at, or slightly above, atmospheric pressure.

Traps 19 (dry ice), 20 (Drierite), 23 (copper oxide wire cooled with dry ice), and 28 (furnace containing copper wire, and silver wool at 420°C) are used to remove final traces of water. The silver wool in this latter furnace removes any halides present. Trap 21, which is a 2 L round-bottom flask, has a large surface area, thereby making it an efficient CO_2 collector at liquid nitrogen temperatures. Radon removal is carried out, when necessary, using the principle of fractional distillation described by de Vries (1957). The radon removal trap (25) consists of two concentric copper tubes with a 4 mm air annulus between them, the innermost tube (41 mm O.D.) forming part of the vacuum system. The outer tube (49 mm I.D.), is kept at the temperature of liquid nitrogen during the radon removal, and the 4 mm air space provides the required temperature gradient to the inner tube. The connecting lines of the "Collection/Storage, Inorganic Reaction, and Purification Systems" (Fig. 8) are pyrex glass with vacuum-cup stopcocks to permit operation under vacuum as well as at pressures above atmospheric pressure.

The section of the system between positions 15 and 24 is evacuated with a fore pump only, producing a vacuum of about 10^{-3} mm Hg. The final purification section (Fig. 8, 9) is evacuated by a fore pump and a mercury diffusion pump. A vacuum of 10^{-6} mm Hg can be achieved in this section but routine operation at 10^{-4} mm Hg produces satisfactory results.

All gaseous samples are now stored in Hoke metal cylinders (27), one of which is shown being cooled with liquid nitrogen in the bottom right of Figure 9. Experience has shown that CO_2 can be kept in these cylinders for periods of up to 6 months without becoming "dirty". The use of metal cylinders for storage and transportation has the distinct advantage of almost entirely eliminating the possibility of accidents in the laboratory, which are not uncommon with glass storage systems.

Counter Filling System

Portions of the 2 L and 5 L counter filling systems are shown in Figure 10. The sample counters are permanently attached to the filling systems and are located to the right of the figure. Vacuums of 10^{-6} mm Hg are achieved by use of a fore pump and a large mercury diffusion pump. Both counter filling systems are joined to the same pumping system. Routinely the 2 L counter is filled to a pressure of 150 cm at 26°C and the 5 L counter to a pressure of 75 cm at 26°C. Counting characteristics are temperature dependent. Changes in room temperature, however, are compensated for by adjusting the pressure accordingly. Counter filling pressures are measured on Heisse Bourdon Tube gauges (Fig. 10).

PREPARATION AND MEASUREMENT OF THE SAMPLE

Sample Type and Treatment

Theoretically, any material, organic or inorganic, which contains radioactive carbon and whose age falls within the range of "modern" to approximately 50 000 years old can be dated by the radiocarbon method. The most common materials submitted for dating, however, are wood, charcoal, peat, lake sediments, bones, soils, and shells.

Labelling, recording, physical examination, removal of extraneous matter such as rootlets in charcoal, or silt on shells, and drying of samples not processed immediately upon submission to the Laboratory are routine, though time consuming operations to which all samples are subjected. The cleaning (treatment) process used depends on the type of sample to be dated. The object of the treatment is to remove carbon-containing material that was NOT part of the sample when the carbon was withdrawn from the dynamic carbon reservoir (i.e. up to the time of death) and incorporated into the material under study. Examples of this

CARBON DIOXIDE COLLECTION/STORAGE SYSTEM

21. COLLECTION FLASK (2000 mL) — liquid nitrogen
22. MEASURING/STORAGE FLASKS (3×5 L flasks)

PURIFICATION SYSTEM

23. TRAP with copper oxide wire and dry ice
24. FILTER, fritted glass
25. FRACTIONATION FLASK (copper) — liquid nitrogen
26. COLLECTION FLASKS (80 mL) — liquid nitrogen

27. CYLINDER, stainless steel (175 and 300 mL)
28. QUARTZ U-TUBE with copper wire and silver wool at 420^C
29. CYLINDER of HYDROGEN
30. "BREAKOFFSKI" for 13C
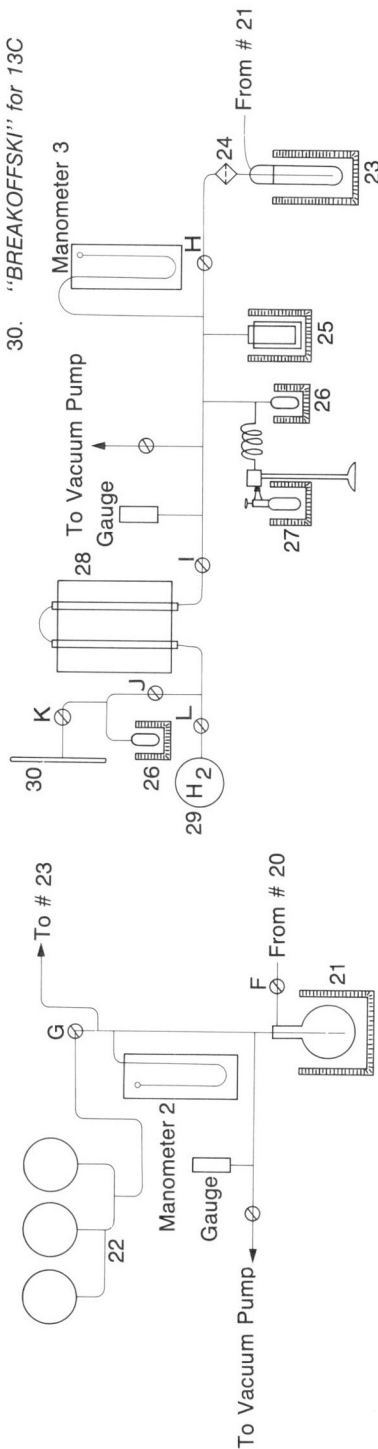
LEGEND

⊘ Stopcock

⊔ Dewar Flask

＊ Additional Bubble Trap in the line
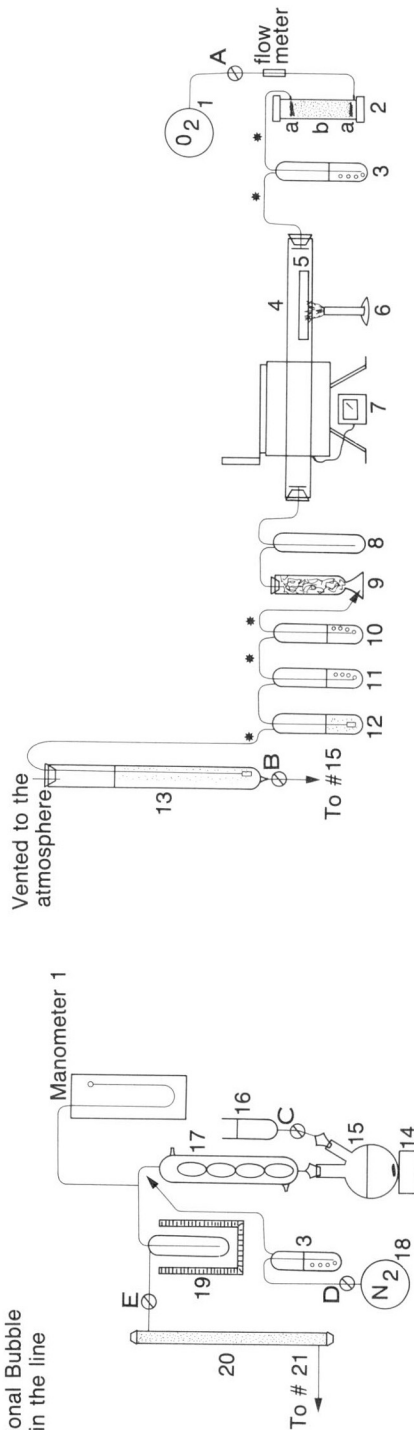
INORGANIC REACTION SYSTEM

14. Magnetic stirrer
15. REACTION FLASK, 2000 mL
16. BURETTE with phosphoric acid
17. CONDENSER
18. Cylinder of NITROGEN
19. TRAP — dry ice
20. DRYING COLUMN with DRIERITE

ORGANIC COMBUSTION SYSTEM

1. Cylinder of OXYGEN
2. ADSORPTION BOTTLE: (a) Drierite
                        (b) Ascarite
3. BUBBLE TRAP with sulphuric acid
4. QUARTZ COMBUSTION TUBE
5. SAMPLE BOAT
6. Gas BURNER

7. COMBUSTION FURNACE with copper oxide at 650°C
8. BUBBLE TRAP for water
9. ADSORPTION BOTTLE with glass wool
10. BUBBLE TRAP with silver nitrate
11. BUBBLE TRAP with chromic acid
12. BUBBLE TRAP with chromic acid and fritted bubbler
13. BUBBLING COLUMN with potassium hydroxide and fritted bubbler

GSC

Figure 8. Carbon dioxide preparation and purification system.

11
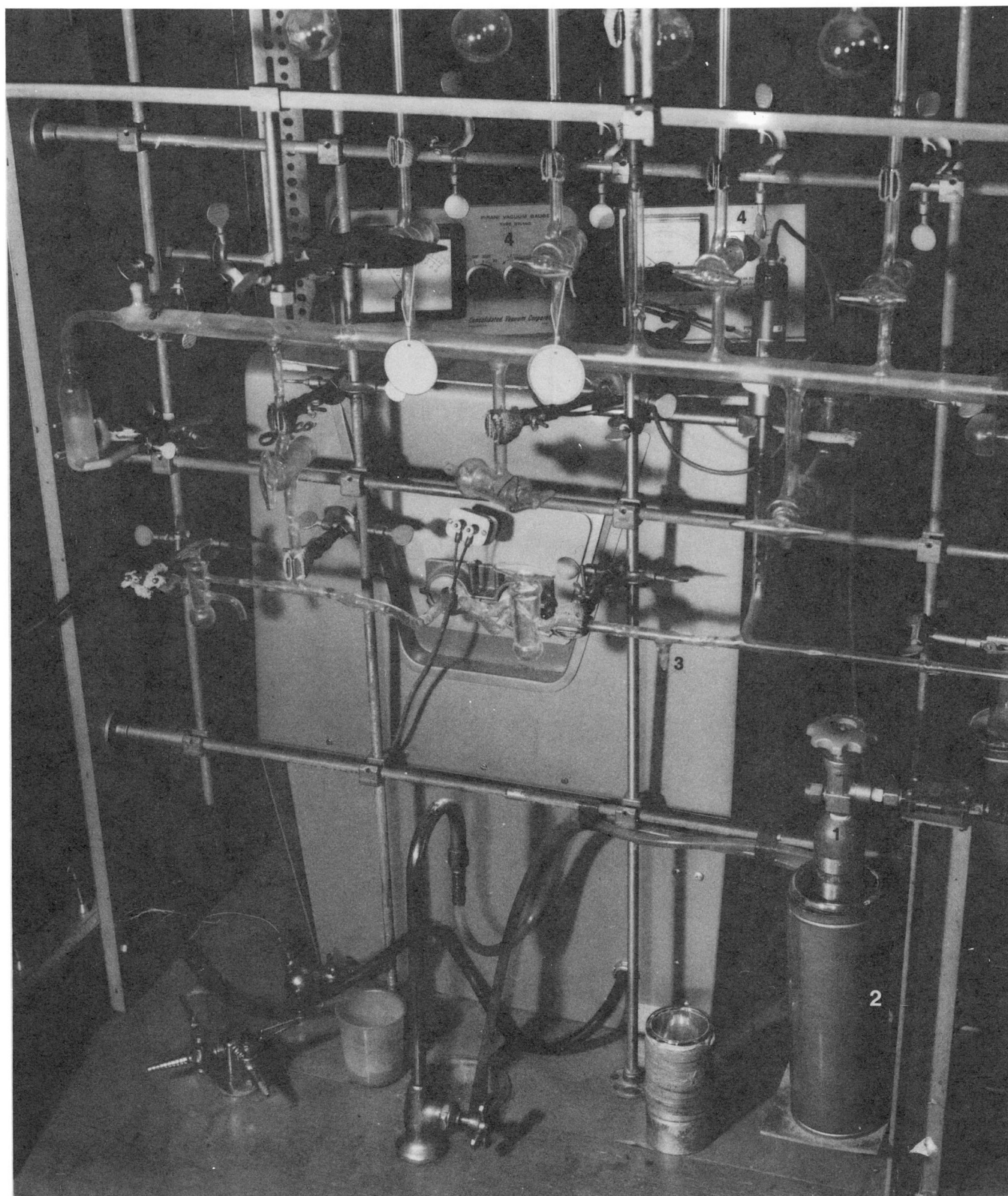
1. Sample storage cylinder   3. Sample purification furnace
2. Liquid nitrogen container   4. Vacuum gauge

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Figure 9. *Part of the gas purification system.*

→ To counters

Figure 10. *The counter filling systems.*
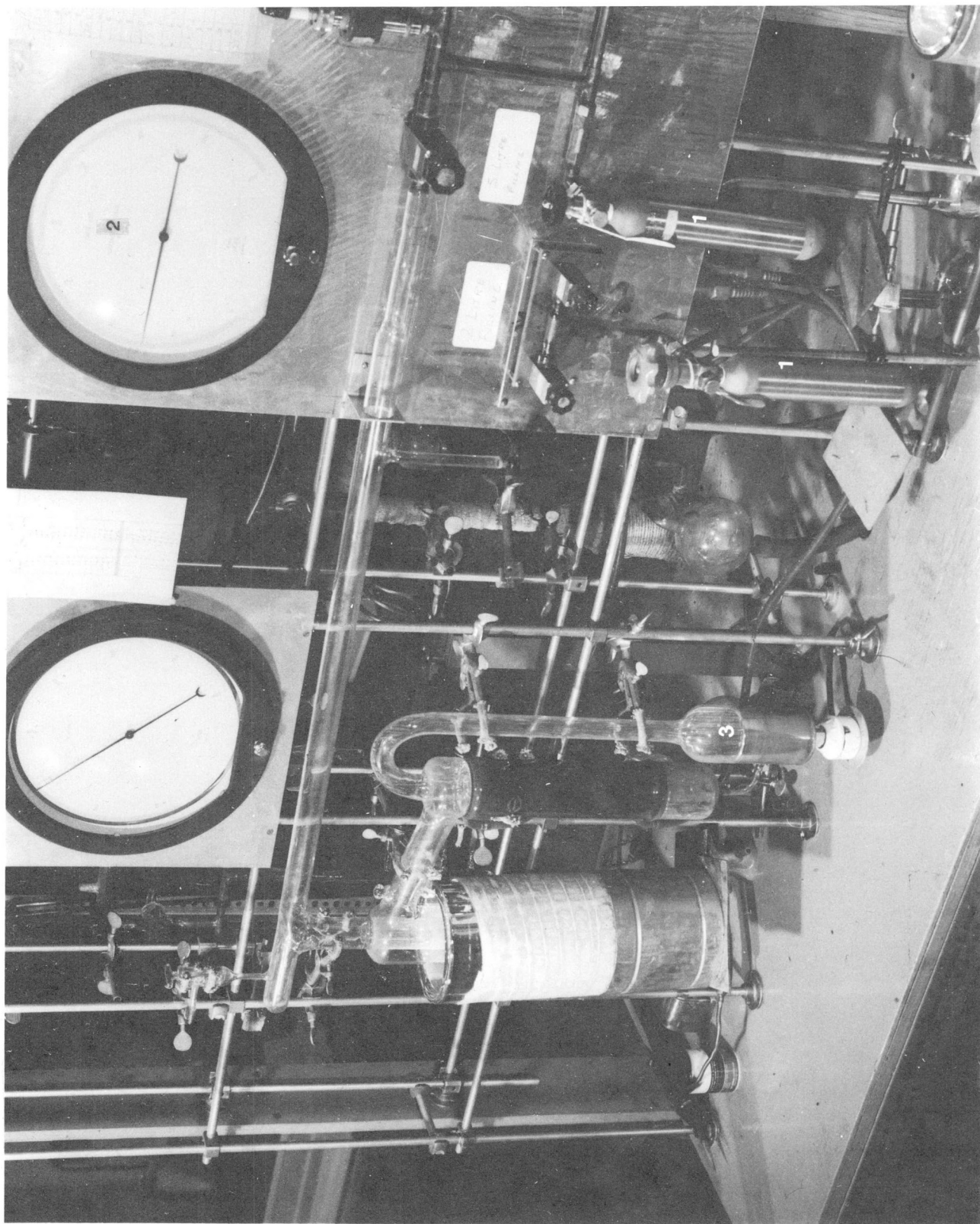
1. Sample Storage Cylinders

2. Heisse Bourbon Tube
   Pressure Gauge

3. Mercury Diffusion Pump

type of sample contamination are humic acids in wood and peat samples; modern rootlets in peat, charcoal, and lake sediments; or inorganic carbonate in organic samples. The standard treatment of different types of materials is described below. The standard treatment (ST) may vary depending on the composition of the sample.

Wood samples are usually scraped and cut into small splinters. These are then treated for 30 minutes in a hot base solution (1% NaOH) to remove humic acids, then for 30 minutes in hot acid (2 N HCl) to remove carbonates, and finally rinsed in hot distilled water. The treated sample is then dried in an oven at 105°C. Well preserved charcoal, peat, and lake sediment samples with a fibrous structure are given the same treatment as wood. Some charcoals, peats, and lake sediments, however, are appreciably soluble in hot base, and in these cases the base leach is either reduced to 5 minutes in cold base (CB) or may be omitted completely. The base leach is always omitted when dealing with soil samples.

Bone samples are crushed to as small a size as possible, preferably to a powder, and then treated with acid (3 N HCl) until all the carbonate fraction has been removed. Certain bones will not react with this acid, probably because of their dense structure, and in these cases more concentrated acid (6 N HCl) is used. After effervescence ceases, the remaining material is washed thoroughly with distilled water, treated with base (0.1 N NaOH) for between 30 and 60 minutes, washed again with distilled water, and dried. If the organic (collagen) fraction of the bone is soluble in base, the base treatment is omitted.

Shell samples are washed in water to remove foreign material such as sand, and if the shells are large enough, they are cleaned with a stiff brush. Then a thin outside layer of the shell is removed with dilute hydrochloric acid in order to remove any possible surface contamination. The amount of shell removed depends largely on the size of the sample submitted but the standard treatment is to remove the outer 20% of the shells.

Sample Requirements

It is important that an adequate amount of sample be collected and submitted to the laboratory in order that an age determination can be carried out under optimum conditions (i.e. without the necessity of having to mix the sample gas with "dead" gas for counting purposes). The desired amounts of <u>dry</u> sample differ from one type of organic material to another depending on the amount of carbon each contains, the state of the sample, the conditions that have affected the sample in situ, and the treatment that the sample must undergo in the laboratory prior to counting. Table 2 lists the minimum amount of dry material that is required for the 2 L counter operating at 2 atmospheres pressure and the 5 L counter at 1 atmosphere.

The relatively large spread in the amount of sample required for peats and lake sediments is because of the natural variability in the samples submitted. It is also difficult to accurately estimate the amount of bone sample required. In general, the amount of collagen in a fossil bone disappears as a function of time so that the older the bone the more sample is required. Also, fossil bones that have been subjected to wet conditions prior to collection contain less collagen than those that have been buried in arid regions. It should be emphasized that anyone collecting samples, of any type, for future age determination should endeavour to collect as much sample as possible and, in any case, try to collect at least twice as much as the minimum required. This latter ensures that, if necessary, a duplicate age determination can be carried out on the same sample material.

Table 2. Sample weights required for dating

| Sample Type | Minimum Amount of Dry Sample (g) | |
	2 L Counter (2 atm)	5 L Counter (1 atm)
Wood	6	10
Charcoal	6	10
Peat	10-25	25-50
Lake Sediment	10-25	25-50
Shell	30	50
Bone	500-1000	1000-1500

Preparation and Purification of CO_2 Gas

Organic Samples

The CO_2 gas preparation and purification line is shown in schematic form in Figure 8. The components of this system have been described previously under *Sample Preparation and Purification System*. The method used to prepare CO_2 is described below. (Numbers in brackets refer to the legend in Figure 8.) For organic samples (wood, peat, bone, etc.), a weighed amount of treated sample is placed in a stainless steel boat (5) and is pushed into the quartz combustion tube (4). After the rubber stoppers and ceramic heat reflectors are inserted into the ends of the combustion tube, oxygen is passed through the system (2 to 13) for approximately 20 minutes in order to flush out the air and also any traces of CO_2 left from the previous sample. The desired gas flow rate is maintained by properly adjusting the flow meter downstream of the oxygen cylinder. The bubbling column (13) is then filled to the 400 mL level with potassium hydroxide (6N). It was previously determined that this volume and strength of potassium hydroxide solution is more than sufficient to absorb all the CO_2 produced for sample sizes required to fill the 2 L and 5 L counters to their routine operation pressures. In order to ensure that any carbonate present in the potassium hydroxide solution is removed prior to use, strontium chloride ($SrCl_2 \cdot 6H_2O$) is added at a rate of 5 g/L of solution. Any strontium carbonate formed precipitates and is filtered off. The sample is ignited by means of a burner (6). The CO_2 produced from combustion passes over hot (650°C) copper oxide wire in the tube furnace to ensure complete combustion and eventually bubbles through the column (13) where it forms carbonate in the solution. After the combustion is completed, oxygen is passed through the system for an additional 10 minutes. The resulting hydroxide-carbonate solution is then drained into a 2000 mL flask (15). Prior to adding the solution, the flask is flushed with dry nitrogen (18) to remove the air. The glass line between the flask (15) and stopcock H, and including the three 5 L storage flasks (22), is now evacuated by the vacuum pump. After a suitable vacuum is obtained, stopcock G is closed. Trap 21 is cooled with liquid nitrogen. Phosphoric acid is now slowly added to the hydroxide-carbonate solution through stopcock C and the resulting CO_2 is collected in the collection flask (21). After the reaction is finished, stopcocks E and F are closed, G is opened, the liquid nitrogen is removed from the collection flask, and the CO_2 is allowed to expand into the three 5 L flasks (22). The gas yield is then measured by reading the pressure on the mercury manometer. After the section of the line between stopcocks H and K has been evacuated by means of a diffusion and vacuum pump, stopcock I and the vacuum stopcock are closed, stopcock H is opened, and the CO_2 gas transferred to a steel cylinder (27) cooled with liquid nitrogen. The cylinder is removed from the system and stored until required. One or two days before the gas is to be counted, final purification is carried out by placing the cylinder on the line, evacuating the system between stopcocks H and K, and passing the gas through the furnace containing copper wire and silver wool at 420°C (28). The hot copper wire in this furnace is regenerated between sample preparations by passing pure hydrogen gas (29) over it.

As previously stated, this method of preparation and purification of CO_2 from organic samples has been used routinely in the laboratory since October 1976. The method has proven time saving as the number of passes through the copper-silver furnace (28) required to obtain optimum counting characteristics has been greatly reduced. Prior to accepting this method as routine, however, a set of samples originally prepared by the previous method was subjected to the new preparation technique. A comparison of the results obtained is shown in Table 3. In all cases the ages agree within the experimental error. As pointed out in the footnote to Table 3, the $\delta^{13}C$ determinations were carried out by either the Geological Survey of Canada or the University of Waterloo. The latter results were all obtained at the same time and when they were compared with those of Geological Survey of Canada it was evident that, in all cases, the Waterloo results were more negative. Originally it was felt that isotopic fractionation during preparation was the cause of the differences but the $\delta^{13}C$ results for GSC-1097, which was prepared by both methods, agreed because both determinations were made by Waterloo. The discrepancy was finally explained when it was discovered (R.J. Drimnie, University of Waterloo, personal communication, 1977) that the two laboratories involved were using slightly different methods for calculating the carbon isotope ratios.

Inorganic Samples

Samples composed mainly of carbonate (e.g. shells, marl) are placed directly into the 2000 mL flask (15) with about 1 L of distilled water. After evacuating the system, the shell-CO_2 is released by addition of concentrated phosphoric acid. Subsequent steps are the same as described above for organic samples.

Counting the Sample

The ^{14}C concentration of samples is measured in one of the proportional counters described earlier in this report. Experience has shown that, at least theoretically, the following daily sequential procedure is satisfactory for counting: background, unknown sample, unknown sample, standard, unknown sample, unknown sample, background, ... etc. However, when a background or standard count would fall 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 count is used twice – at the end of one month and at the beginning of the next) for the monthly age calculations.

Counting periods during the week are approximate 1200 minutes (termed a 1-day count) and on weekends are 4200 minutes (3-day count). Unknowns are counted once if it is a weekend count, twice if counts are of one day duration, and more often if the statistical analysis of the counting rates reveals greater than random fluctuations. For unknowns that are given two 1-day counts, the second count is scheduled, where possible, approximately two weeks after the first count.

The 2 L counter is filled to a pressure of about 2 atmospheres (150 cm Hg at 26°C). Changes in the "castle" temperature are corrected for by changing the pressure correspondingly. Samples that are too small to fill the 2 L counter to 2 atmospheres are mixed with background ("dead") 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.

Table 3. Comparison of results obtained by different sample preparation techniques

Sample Number	Material	Preparation Technique*	Uncorrected Age (BP)	$\delta^{13}C$** (°/₀₀)	Corrected Age (BP)
GSC-1097	Wood	Old	8 670 ± 70	-24.6(WAT)	8 680 ± 70
-1097-2		New	8 730 ± 80	-24.6(WAT)	8 730 ± 80
GSC-1496-B	Whale bone	Old	9 080 ± 80	-15.9(GSC)	9 320 ± 80
-1496-C		Old	9 260 ± 90	-15.4(GSC)	9 410 ± 90
-1496-3		New	9 200 ± 80	-16.6(WAT)	9 340 ± 80
GSC-1498	Whale bone	Old	7 110 ± 80	-15.2(GSC)	7 260 ± 80
-1498-3		New	7 110 ± 80	-16.4(WAT)	7 240 ± 80
GSC-1748	Whale bone	Old	8 940 ± 90	-16.8(GSC)	9 070 ± 90
-1748-2		New	8 820 ± 90	-17.1(WAT)	8 940 ± 90
GSC-1760	Elephant tusk	Old	21 800 ± 320	-20.5(GSC)	21 900 ± 320
-1760-2		New	21 600 ± 230	-21.1(WAT)	21 600 ± 230
GSC-1813	Peat	Old	4 940 ± 60	-23.1(GSC)	4 970 ± 60
-1813-2		New	4 900 ± 60	-24.6(WAT)	4 900 ± 60

* "Old" preparation technique refers to the routine method used prior to October 1976 and "New" refers to that used since then.

** The $\delta^{13}C$ determinations were carried out by two different laboratories. "GSC" refers to the Geological Survey of Canada Geochronology Section.
"WAT" refers to the Department of Earth Sciences, University of Waterloo, Waterloo, Ontario.

The 5 L counter is operated routinely at about 1 atmosphere (75 cm Hg). The majority of samples are not large enough for higher 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 has accumulated, the counter is calibrated at 4 atmospheres. In order to obtain the best possible age determination on old samples run at high pressure, these samples are usually counted for a 5-day period. High pressure work is time consuming, firstly because of the longer time involved in preparing the larger volume of gas required, and secondly because of the greater gas purity required at high pressure. The latter need is due to the increase in the concentration of electro-negative impurities with increased pressure. Over the years a number of samples have been counted in the 5 L counter both at 1 atmosphere and 4 atmospheres pressures (Table 4).

As mentioned previously, in order to obtain satisfactory counting characteristics, a sample must be free of electro-negative impurities (e.g. water vapour). In order to check sample purity prior to counting, a pitchblende source is placed near the newly filled counters, the counter voltages are set near the midway point on the steeply rising portion of

the response curve, and the counting rates recorded. Shifts in the operating point, reflecting changes in the concentration of electro-negative 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 operating voltage is adjusted accordingly.

Background and Contemporary (Modern) Standard Gases

As discussed previously, every radiocarbon dating laboratory has a "built-in" background which must be measured before an unknown sample count can be determined. In order to measure this background, the counters must be filled with "dead" CO_2 gas (i.e. gas that contains no measureable amount of ^{14}C). The materials this laboratory uses to produce background gases are Precambrian limestone (inorganic) and Pennsylvania anthracite (organic). No treatment is carried out on these materials and the gases are prepared and purified as described previously. The samples are counted alternately in the 2 L and 5 L counters approximately once a week. As well as providing an average monthly background for age calculation, this technique also serves as a check that all counting equipment is working satisfactorily.

By convention, the modern standard activity used by most ^{14}C laboratories is taken as 95% of the activity of the National Bureau of Standards (USA) oxalic acid standard. This 95% oxalic acid activity has been established as the most probable value for the undisturbed assay of modern (1950) wood, unaffected, that is, by the "Suess" and "bomb" effects. It does not, however, remove the uncertainties due to isotopic fractionation or the variations that have occurred in the radiocarbon concentration in the atmosphere in the past. The adoption of the 95% oxalic acid counting rate does, however, lead to a standardization of the reported results.

AGE CALCULATION AND ASSIGNED ERROR

Age calculations are presently being carried out on a CDC Cyber 730 computer. Calculations are based on a ^{14}C half-life of 5568 ± 30 years and 95% of the activity of the NBS oxalic acid standard. Ages are quoted in radiocarbon years before present (BP) where "present" is taken to be 1950.

Since January 1973 the error assigned to each age has been calculated using only the counting errors of sample, background, and standard, and the error in the half-life of ^{14}C (Lowdon and Blake, 1973) Lowdon et al., 1974. Prior to 1973 an error term to account for the average variation of approximately ±1.5% in the ^{14}C concentration of the atmosphere during the past 1100 years (due to change in cosmic radiation intensity or climatic change) had been incorporated in the age error calculation. This last error term had been used mainly as a result of the work done on Douglas Fir (**Pseudotsuga menziessi**) by Dyck (1965, 1966, 1967) and Sequoia (**Sequoia giganter**) by Willis et al., (1960). More recent work on bristlecone pine (**Pinus aristata**), however, mainly by the University of Arizona but also by the University of Pennsylvania and other laboratories has shown that the concentration of ^{14}C in the atmosphere has varied by as much as 15% over the past few thousand years. Sufficient data are now available to provide a conversion table from radiocarbon years to tree ring (calendar) years for the last 7500 years, if the user so desires (Olsson, 1970; Damon et al., 1972). These data take into account the variations in the ^{14}C concentration in the atmosphere. For this reason it was decided, starting in January 1973, to omit the correction for fluctuations in the concentration of atmospheric ^{14}C from Geological Survey of Canada

Table 4. Comparison of ages at different pressures in the 5 L counter

Sample Number	Length of Count (days)	Pressure (Atmospheres)	^{14}C Age (BP)
GSC-993	3	1	>37 000
-993-2	4	4	46 400 ± 940
GSC-1002	1	1	>40 000
-1002-2	5	4	>48 000
GSC-1019	2	1	>40 000
-1019-2	5	4	52 200 ± 1760
GSC-1798	3	1	>38 000
-1798-2	4	4	>51 000
GSC-1864	3	1	>43 000
-1864-2	6	4	>49 000
GSC-2010	5	1	>42 000
-2010-2	4	4	>50 000
GSC-2094	4	1	>44 000
-2094-2	4	4	>49 000
GSC-2218	3	1	>42 000
-2218-2	5	4	>56 000
GSC-2234	6	1	>39 000
-2234-2	5	4	53 100 ± 1560
GSC-2353	3	1	>39 000
-2353-2	5	4	45 200 ± 630
GSC-2373	4	1	>43 000
-2373-2	5	4	51 900 ± 1350
GSC-2394	3	1	>39 000
-2394-2	5	4	>54 000
GSC-2559	3	1	>40 000
-2559-2	5	4	>51 000
GSC-2627	5	1	>39 000
-2627-2	5	4	>48 000

radiocarbon dates. It should be noted that omission of this error term in no way affects the date produced, but it does reduce the error term assigned to a date.

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, auxiliary scalers, and Esterline-Angus recorder. Only counts inside the probability range, as predicted from the randomness of radioactive decay, are accepted. For example, if one of three measurements of the same sample is more than 2σ removed from the average, it is rejected. The standard deviation (σ) of a single measurement is the square root of the number of counts divided by the 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 is acceptable because statistics theory permits a total deviation of 4σ from the average of three measurements. Weekend counts are divided into 10 hour intervals and treated statistically using the two out of three σ-criterion before they are accepted.

The age of a sample is calculated by means of a formula (using the ^{14}C half-life (HL) of 5568 years) derived from the radioactivity decay law:

$$t = HL/\ln 2 \cdot \ln \frac{Ao}{A}$$

or

$$t = 18.5 \times 10^3 \log \frac{Ao}{A}$$

where: t = age of the sample in years
Ao = specific activity of the modern standard (95% of the NBS oxalic acid specific activity)

and A = specific activity of the sample.

The accepted way of reporting ^{14}C results is to state a time range, a period within which the ^{14}C age will fall with a certain probability, in the form

Age ± Error (in years)

A ^{14}C age must never be dissociated from its error term. Both must be quoted when reporting and applying results.

The stated error is derived from considerations of the random nature of radiocarbon decay and is therefore affected by uncertainties in the determination of the background, standard, and unknown sample. The error is further dependent on sample activity. A young sample (i.e. high activity) will have a smaller error than an old sample (i.e. low activity). There is some variation in the practice of laboratories in computing errors and, as a result, it is essential that anyone wishing to use ^{14}C ages from different laboratories should determine the procedure used by these laboratories. Many radiocarbon dating laboratories publish their procedures in the journal *Radiocarbon*. Whereas a majority of laboratories use one standard deviation (1σ) in calculating errors for finite ages, the Geological Survey of Canada Radiocarbon Laboratory has always used 2σ. Using this 2σ criterion means that there is a 95% chance that the true radiocarbon age will fall within the indicated limits; using 1σ means that there is only a 68% chance of this occurring. For infinite, or "greater than", ages this laboratory uses 4σ which enables one to say that there is a 99.9% chance that the radiocarbon age is in fact greater than that given.

ISOTOPIC FRACTIONATION

Isotopic fractionation means that differences from the natural abundances of the three carbon isotopes (^{12}C, ^{13}C, and ^{14}C) have developed as a result of various biological processes in nature. These differences show up as variations in the ^{13}C/^{12}C ratio and the ^{14}C/^{12}C ratio in organisms. The former can be measured by a mass spectrometer and the latter calculated using the fact that the ^{14}C/^{12}C ratio is almost exactly twice that of the ^{13}C/^{12}C ratio. A 1% variation in the natural ^{14}C concentration of materials is equivalent to 80 years on an age calculation.

As discussed earlier, not all samples dated in this laboratory are corrected for isotopic fractionation. When ^{13}C/^{12}C ratios are obtained, however, a correction for fractionation is applied to the date. When corrected dates are published they are always accompanied by the δ^{13}C value. The "normal" values relative to the Pee Dee Belemnite (PDB) standard used for correction are δ^{13}C = -25.0°/$_{oo}$ for wood, terrestrial materials, and bones (both terrestrial and marine); and 0.0°/$_{oo}$ for marine shells.

Practically all radiocarbon laboratories which apply isotopic fractionation corrections to their dates make a correction for marine shells based on the value δ^{13}C = -25.0°/$_{oo}$. Although it has previously been stated (Mangerud, 1972; Jardine, 1978) that it is important that publications include not only the determined age of a shell sample, but also a description of the methods used in determining the age, it is my opinion that, only too often, users of these ages ignore the latter consideration, and that the use of the -25.0°/$_{oo}$ correction factor only confuses the issue. In fact, the best procedure when dealing with shell ages might be to publish only the uncorrected age, accompanied by the δ^{13}C value. The reason for this opinion is as follows. Marine shell ages may be influenced by the following known effects (Jardine, 1978):

1. isotopic fractionation, leading to an enrichment in ^{14}C activity (Krog and Tauber, 1974);

2. isotopic replacement after death by dissolved CO_2 in groundwater, etc;

3. initial ^{14}C activity of the sea water in which the animal lived;

4. hard-water effect when bicarbonate derived, in part, from old, inert sources is used in constructing shells.

The only one of these four effects that can be determined with any degree of certainty is isotopic fractionation (which, in the case of marine shells, approximates 400 years when based on the factor -25.0°/$_{oo}$), and it does not seem feasible that only one out of four possible corrections should be applied. It is for this reason that the policy in this laboratory has always been to make only the correction necessary to take into account the slight fractionation between the shells and the PDB standard.

CONCLUSION

Although the principal objective of the Geological Survey of Canada Radiocarbon Dating Laboratory, Terrain Sciences Division, is to supply the best possible radiocarbon ages on carbonaceous and calcareous materials of geological interest to officers of the Geological Survey of Canada, the work also involves research into factors relating to the accuracy and reliability of the dating method and into sample contamination problems. Problems of this nature which have been, and in some cases are continuing to be, investigated include the following:

- a study of contamination in marine shells by dating different fractions of the shell;

- a study of contamination in peat and soil samples by dating different humic fractions;

- a study of coeval organic-inorganic pairs to determine the possible effects of environmental conditions on different types of material;

- investigations into different methods for extracting collagen from bone samples for the dating purposes;

- a study of variations in the ^{14}C concentration in the atmosphere prior to 1950; and

- investigations into the variations in ^{14}C concentration in the atmosphere at the present time as a result of thermonuclear testing.

The laboratory also carries out, when requested, an exchange of specific samples (usually wood) with other radiocarbon laboratories for purposes of checking the dating methods.

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