Apparatus for Carbon-14 Dating

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THROUGH the collaboration begun at the end of 1951 between the Physical and Geochemical Institutes of the University of Rome, a laboratory is now ready to begin its dating activity by the carbon-14 method. The object of this paper (*1*) is to describe the characteristics and working of the apparatus, which is now complete, and which was only briefly mentioned in an earlier note (*2*) when it was still in the development and testing stage.

We wish to state beforehand that the method used in this laboratory is fundamentally the same as that developed by W. F. Libby and his colleagues (*3, 4*) that is, we carry out measurements on elementary carbon in a screen-wall counter. However, several important modifications have been made in the technique of preparing the radiochemically pure carbon, and in particular in the technique of measuring the radioactivity of the C^{14} isotope with the development of a four-element counter. This arrangement allows the simultaneous measurement of four samples of different specific activity. As will be seen, this procedure tends to eliminate some possible systematic errors of measurement.

Preparation of samples. The preparation of radiochemically pure elementary carbon from materials of animal or vegetable origin follows the main ideas of the method developed by Libby and his colleagues (*3, 4*). We have made no fundamental modifications in the cycle of chemical reactions involved in this method; however, we have found it useful, from the beginning of our experiments, to make several important modifications in the technique, thus obtaining a somewhat different apparatus from that used by Libby *et al.* Our most important modifications are as follows.

1) In experimenting with noncarbonized materials (for example, wood), a carbonization is carried out by heating the sample in a closed crucible, followed by treatment with hydrochloric acid.

In carrying out the first reaction cycle (that is, combustion of the sample in a current of oxygen, reaction of the carbon dioxide thus produced with aqueous ammonia solution, and precipitation of calcium carbonate by addition of calcium chloride) we eliminated the liquid nitrogen "traps" used by Libby *et al.* to solidify the carbon dioxide before passing it into the ammonia solution. We consider this operation superflous; it does not contribute to the purification of the carbon dioxide nor does it seem to be particularly useful for regulating the absorption of this gas in the ammonia solution. In fact, if the carbon dioxide is passed directly into the ammonia solution, the oxygen current being suitably regulated, a regular and complete absorption with an almost theoretical reaction yield is obtained. This was verified by absorbing carbon dioxide produced from very pure calcium carbonate.

The simplified apparatus consists of (i) an oxygen source, (ii) bottles for purifying and drying the oxygen, (iii) an electrically heated quartz combustion tube, (iv) a second quartz tube containing filings of oxidized copper mixed with lead chromate and with silver gauze for completion of combustion, (v) additional bottles for purifying and drying, (vi) bulbs of Jena glass containing aqueous ammonia solution in which the absorption of carbon dioxide and the precipitation and washing of calcium carbonate takes place.

2) The second reaction cycle consists in producing carbon dioxide by treating the calcium carbonate prepared in the first reaction cycle with hydrochloric acid and reducing it to elementary carbon by means of metallic magnesium. This cycle is not carried out at reduced pressure. This involves considerable simplification and modification of the apparatus, which consists essentially of a Kipp's apparatus containing the calcium carbonate and hydrochloric acid connected by bottles for washing and drying to one end of an electrically heated stainless steel tube containing magnesium, at the other end of which is a stopper furnished with a tap. The tap is kept open, and a slightly lowered pressure is maintained across it during the preparatory stage, that is, before starting to heat the tube. In this way the whole apparatus is first filled with air free of carbon dioxide and suitably purified of radon, and then it is filled with the carbon dioxide produced in the Kipp's apparatus.

With this simple apparatus, when the reduction reaction ($2Mg + CO_2 \rightarrow 2MgO + C$) is started by the heating, an automatic but controllable flow of carbon dioxide is set up from the Kipp's apparatus to the steel tube; this flow proceeds regularly with the reaction and ceases when the reaction ceases. The reaction can be made to occur rapidly and we consider its yield, about 85 percent of the theoretical, to be satisfactory.

3) To eliminate the magnesium oxide and excess metallic magnesium obtained during the reduction reaction, we kept the procedure suggested by Libby practically unchanged. We found it convenient, however, to prolong the period of digestion in boiling concentrated hydrochloric acid and to alternate three treatments with this acid with thorough washing with distilled water and partial drying of the sample. By following this procedure we almost always obtain carbon with a satisfactorily low ash content, varying between 2 and 0.5 percent. The final drying of the carbon takes place at 125°C and the sample, still hot, is put in a hermetically sealed bottle for storage.

The sample is ground in an agate mortar that is placed in a kind of transparent, hermetically sealed box. The operator puts his hands, protected by gloves, into this box. The samples are ground and the ash and carbon content are determined at the time when the samples are taken out of the box to be spread on the sample holders of the counter. This last operation is particularly laborious because of the special form of the sample holders.

4) As already indicated, this method for carbon dating involves relative and simultaneous measurements of the activity of four different samples. It is therefore necessary to prepare the four samples in experimental conditions as nearly identical as possible, and, in particular, to have available beforehand a single quantity of each reagent that will be sufficient for all the four preparations.

Of the four samples used, two are to be dated; the activities of these two are compared with those of the remaining two samples, one of which is active carbon prepared from contemporary charcoal, and the other of which is old inactive carbon prepared from a very pure metamorphic crystalline saccharoid limestone (white marble from Carrara) of Secondary Era, attributed today to lower Lias. This limestone is subjected to the same chemical cycle of purification to which all the materials containing carbon are subjected, except, of course, that a hydrochloric acid treatment in the Kipp's apparatus is substituted for the initial combustion. The carbon prepared from this limestone was shown, in a control experiment, to be as inactive as carbon prepared from anthracite. We prefer to use it because the preparation is much simpler.

Method of counting and dating. The counting arrangement (Fig. 1) consists of a Geiger counter with four elements, facing each of which is one of the four samples. Each element is followed by a recording channel. The cylindrical armature constituting the four elements can rotate about its axis *A*; another fixed cylindrical armature, coaxial with the first and supporting the samples, ensures that the latter face the four elements of the counter.

On the sample holder cylinder samples of active and inactive carbon, and two samples to be dated, are mounted on copper supports. Each channel measures the activity of one of the samples, and the pulses of the four channels are recorded contemporaneously on four mechanical counters. By rotating the cylinder about its axis at equal time intervals, all four samples are brought one after another to face each element of the counter. Each channel thus gives data sufficient for dating the samples of unknown ages, and the four values obtained for each of these ages must coincide within experimental error before they are used to obtain a final mean value.

As Crane has clearly shown (*5*), the dating method based on comparing the activity of an unknown sample with the activity of both an active and an inactive sample has an important advantage over Libby's classical method because it eliminates the necessity of knowing the absolute efficiency of the counter and of being sure of the constancy of its characteristics between one run and another. The method used by Anderson *et al.* (*6*) does not compare the activity of an unknown sample with the activity of both an active and an inactive sample in each run, but, like our arrangement, it allows dating on several independent channels.

Four-element grid counter and recording apparatus. Figure 1 shows a schematic section of the four-element grid counter. The relative rotation of the sample holder cylinder *P* with respect to the four elements is effected by means of a weight and the movement takes place on ball bearings. The walls *W* separating the elements are 0.1 mm thick, that is, thick enough to absorb all the electrons emitted by the C^{14}. The area covered by carbon is 450 cm², so that 9 g of carbon are sufficient to give a layer of infinite thickness.

The filling of the counter consists of argon and butane: the partial pressure of the butane is 1 cm-Hg and the total pressure of the mixture is 10 cm-Hg. The butane is commercial grade and the argon is standard grade further purified of oxygen. The grids are maintained at a potential of +45 v with respect to the sample holders. The counter is screened from surrounding radioactivity and from the soft compo-

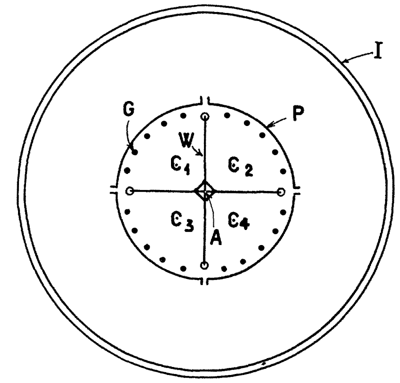

Fig. 1. Schematic section of the four-element grid counter. *I*, external shell; C_1, C_2, C_3, C_4, C^{14} counters; *P*, sample holder cylinder; *G*, grid; *W*, walls separating the elements; *A*, axis.

nent of cosmic rays by a screen of at least 20 cm of iron, and it is screened from the penetrating component of cosmic rays by a complete cover of anticoincidence counters 80 cm in length.

Figure 2 is a block diagram of the apparatus. A quenching circuit Q with a suitable time constant is connected to each of the four Geiger elements and to the Geiger counters of the anticoincidence cover. This prevents the spontaneous onset of a secondary discharge in an element after there has been a first discharge caused by an ionizing particle. The anticoincidence arrangement cannot eliminate these spurious pulses that would disturb the measurements if the quenching circuits were omitted. The circuits A_1, A_2, A_3, A_4, and A_r amplify and invert the pulses. The circuit S emits a pulse every time two or more pulses, each coming from one of the circuits A, enter it simultaneously. Each of the circuits N_1, N_2, N_3, and N_4 operates corresponding mechanical counter every time it receives a pulse from circuit A_1, A_2, A_3, or A_4 not accompanied by a pulse from S. There is, thus, in addition to an external anticoincidence for the cosmic rays, a local anticoincidence of each of the four elements with respect to each of the others. This eliminates both the cosmic ray pulses caused by the imperfect efficiency of the anticoincidence shield and the pulses from electrons created by γ-rays in the counter that pass through the dividing walls between element and element.

The background is 15.5 counts/min. We think that this high background rate is largely the result of the α-radioactivity of the exposed copper surfaces of the counter. It was found that a sample holder of exposed metal is more active than an infinitely thick layer of inactive carbon. The carbon layer eliminates the α-activity of the metallic surfaces. The possibility of reducing the background resulting from this cause is being examined.

Analysis of data. The data furnished by each channel were analyzed in the following way. A camera photographed the mechanical counters at brief regular intervals of time, and the counts registered in each interval were analyzed statistically. This analysis showed that in general the counts obeyed a Poisson distribution, and gave reason to suppose that the fluctuations in counting rate were caused almost entirely by the randomness of the β-decay. Nevertheless in some intervals the number of counts observed was greater than the mean by more than three times the mean square deviation, and the number of such intervals was somewhat greater than that to be expected from a pure Poisson distribution. This effect was attributed to occasional spurious discharges caused by small solid particles deposited on the counter wire. We consider it wise, therefore, to accept only those counts that differed from their mean by not more than twice the mean square deviation. In this way we felt secure that any such spurious discharges would not influence our mean value for the counting rate caused by C^{14} decay electrons; this method produced, in the mean square deviation of the age of the sample, an error of barely 2 percent.

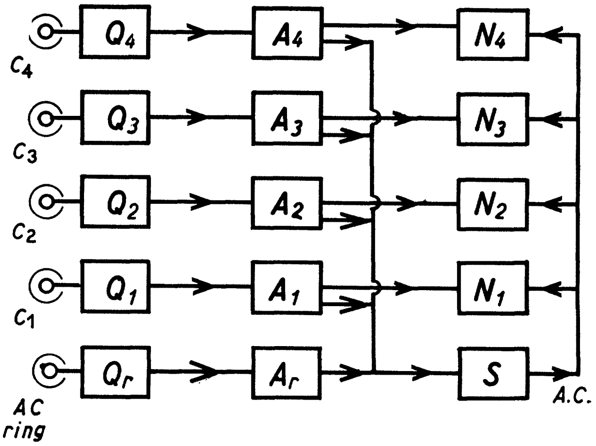

Fig. 2. Block diagram of the counting apparatus. Q, quenching circuits; A, amplifier and inverter circuits; N, operating circuits for mechanical counters; S, local anticoincidence circuit.

Each channel thus gave a value for the age of the sample and the mean of these was taken as the final result; the standard error was calculated from those of the separate values using the Gauss method.

These four separate values, obtained from 12 hr of counting, have always been in excellent agreement among themselves, within the limits of purely statistical error, and we therefore consider that any possible error caused by an imperfect functioning of the apparatus is entirely negligible, and that by increasing the counting time we can reduce still further the standard error of the final result.

The value found for the age is corrected for the different percentages of ash contained in the various samples. It is not necessary to correct for volatile substances adsorbed by the carbon because these, with the method used, would have the same effect on all the samples compared, and this effect is canceled in the analysis of the measurements.

Conclusions. We carried out control measurements using two samples of ages well estimated by other means. One of these samples was prepared from a piece of wood from the Roman ships at the Lake Nemi (Rome), the construction of which is attributed to the Emperor Caligula (A.D. 37–41). The result of our measurement gave 2030 ± 200 yr. The second sample was prepared from charcoal found in an Etruscan tomb near Cerveteri, Italy. The historical age is about 2600 yr. Our measurement gave 2730 ± 240 yr.

These results were obtained after 48 hr of acceptable counting (12 on each channel for each sample) without taking into account the few measurements excluded as having too large a deviation.

Active carbon gives an effect of 5.43 ± 0.12 counts/min above background. This number does not represent an essential datum for us because for each run the count of the unknown sample is compared simultaneously with the count of the active and inactive carbons.

On the basis of the satisfactory results obtained in the control experiments, we think that this technique for measuring the activities, and the modifications introduced in the technique of preparing the samples, as well as the choice of samples of active and inactive carbon for comparison, answer the requirements of the method. A fuller description of apparatus and method will be published elsewhere as soon as we have completed other experiments.

References and Notes

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E. C. Schneider, Pioneer in Aviation Medicine

As a leader in studies of the physiological effects of high altitudes and of the physiology of physical fitness, Edward Christian Schneider became a pioneer in the establishment of modern aviation medicine. Beyond this, however, he was a great teacher of college undergraduates, who have acknowledged his influence not only in their personal tributes to him but also in the records of their careers in the fields of zoology, human physiology, public health, and medicine.

Ed Schneider, as he was familiarly known to his friends, was born (21 August 1874) and brought up in Iowa. He graduated from Tabor College in 1897 and taught there as an instructor in chemistry for 2 years immediately following his graduation. He then entered the graduate school at Yale University to study biochemistry under Lafayette B. Mendel and physiology under Yandell Henderson; he received his Ph.D. degree in 1901. His thesis and first published papers were in the field of biochemistry. Schneider then returned to Tabor College for two more years as professor of biology and physiological chemistry. During this period he married Elsie M. Faurote, who, with his two children and six grandchildren, now survives him.

In 1903 he accepted a position at Colorado College, where he remained for 15 years as head of the department of biology. Here he resumed his researches in biochemistry and also wrote two papers on botanical ecology which resulted from his interests and explorations stimulated by his teaching of botany. Of greater future significance, however, was the beginning, in 1904, of his researches on Pikes Peak on the physiological effects of high altitudes. In 1911 he was a member of the distinguished Anglo-American team, consisting of G. Gordon Douglas, J. S. Haldane, Yandell Henderson, and Schneider, that met in Colorado to continue these investigations. The results of these studies proved to be a landmark in this phase of human physiology.

In 1917, soon after the United States entered World War I, Dr. Schneider was called to Washington, D.C. by the Medical Research Board that had been established by General Gorgas to oversee the development of low-oxygen tests for aviators and later to supervise the physical examination of aviators. For this duty he was first commissioned a captain and soon was promoted to a major in the Sanitary Corps, U.S. Army. The work was shifted to Hazelhurst Field on Long Island, where, under Schneider as officer in charge of physiological research, tests of ability to withstand high altitudes were devised and personnel were trained to administer these tests at flying fields throughout the country. By March 1918 a school for flight surgeons was demanded. Dr. Schneider designed the first curriculum and, in this way, began the development that later led to schools of aviation medicine.

In July 1918 a summons came from General Pershing for men trained in the Hazelhurst School. Thirty-three officers and men headed by a research board of four, of which Major Schneider was a member, embarked on 6 August for service with the American Expeditionary Force. A laboratory was set up in Issoudan in France, with Schneider as officer in charge of physiological work. Here he not only worked in the laboratory but also went on flights with the aviators to experience the actual conditions. It was here that the Schneider test for physical fitness, which became widely used in the selection of aviators, was developed; its use continued through World War II and later. After 6 months in the European theater he returned to Hazelhurst Field and was discharged from service; later he became a lieutenant colonel in the reserve. However, from September 1919 until 1925, he continued in a civilian capacity as director of research at the School of Aviation Medicine that had been established at Mitchell Field.

It was also in 1919 that he accepted appointment as Daniel Ayres professor of biology at Wesleyan University. For 6 years he carried the double load, spending 2 days a week and vacations at Mitchell Field. At Wesleyan he became almost immediately one of the most influential members of the faculty. His teaching was in the fields of elementary biology, bacteriology, physiology, and public health. When the Shanklin Laboratory, of Biology was erected in 1928, many of