The Half-Life of Carbon 14[1]

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The half-life of carbon 14 has been determined by gas counting of $C*O_2+CS_2$ mixtures (where $C*O_2$ is used to designate inert carbon dioxide containing some $C^{14}O_2$) by using pairs of counters that are identical in construction except for the length of the cathodes. The suitability of various equations proposed for calculating the true counting rate, C_T, from the resolving time, t_r, and the observed counting rate, C_o, is evaluated from experimental measurements of C_o and t_r and is presented graphically. A value of $5,370 \pm 200$ years for the half-life of C^{14} is obtained from these measurements. By comparison with the results of other workers, it is estimated that the most probable value for the half-life of carbon 14 is $5,400 \pm 200$ years.

I. Introduction

The half-life of carbon 14 has been the subject of many determinations, the values of which have ranged from a high of 7,200 to a low of 4,700 years. Two general methods have been used: end-window counting of solid barium carbonate, and counting of gaseous carbon dioxide, in which the radioactive carbon is either a minor or a major portion of the filling gas of the counter. In general, larger and more numerous corrections are necessary to the experimental measurements if solid counting is employed.

Libby [1][3] and Jones [2] have introduced the radioactive carbon dioxide as a minor constituent of the gas filling of Geiger-Müller counters containing the customary alcohol-argon mixture. The technique employed by Brown and Miller [3] of counting $C^{14}O_2+CO_2+CS_2$ (abbreviated as $C*O_2+CS_2$) mixtures represents a notable advancement in the analysis of radiocarbon.

The National Bureau of Standards has prepared, and is in the process of certifying, standard sources of activity of C^{14}. The process of standardization consists of three parts: (1) A collaborative determination by mass spectrograph of the isotopic ratio of C^{14} in carbon dioxide prepared at the Bureau from active barium carbonate, (2) conversion at the Bureau of a weighed amount of barium carbonate into active sodium carbonate solution containing 0.1-M inactive sodium carbonate as carrier and approximately 0.0001-M free sodium hydroxide, (3) collaborative analysis of the solution by absolute gas counting. The standards after certification will be available * in the form of glass ampoules containing 25 ml of the above solution and having an activity of the order of 1,000 disintegrations per second per milliliter. A full account of the collaborative analyses will be presented when all the results of the determinations have been received. The purpose of the present paper is to offer preliminary values obtained at the Bureau for this intercomparison.

The value in this paper for the half-life of C^{14} was calculated from the equation

$$T_{\frac{1}{2}}=0.693 \ N/(dN/dt), \tag{1}$$

where N, the number of atoms of C^{14}, was determined by mass-spectographic analysis, and dN/dt (the rate of radioactive decay) was measured by gas counting of mixtures of $C*O_2+CS_2$.

II. Determination of the Number of Active Carbon Atoms

Radioactive carbon dioxide was obtained by heating active barium carbonate[4] to approximately 1,100° C in a quartz tube. Analysis of the isotopic ratio was made by Fred L. Mohler and Vernon H. Dibeler, of the Bureau's Mass Spectrometry Section. The average value obtained from 10 determinations was 3.876 ±0.002 percent of C^{14}, with an estimated accuracy of ±0.04 percent (absolute), based on known limits to calibration and other procedural errors. The probable error was computed from the formula

$$0.8453 \Sigma d/n \sqrt{n-1}.$$

A quantity of active barium carbonate weighing 0.1066 ±0.0001 g was transferred to a small round-bottomed flask containing 1.40 g of inert barium carbonate. (The exact quantity used is not critical.) The mixture was treated with an excess of perchloric acid in an evacuated system and the carbon dioxide absorbed in a tenfold excess of 2-M sodium hydroxide. The large amount of inactive CO_2 evolved aided in sweeping over the active carbon dioxide. (It should be noted that neither the perchloric acid nor the sodium hydroxide were required to be carbonate-free.) Quantitative transfer was accomplished by boiling the acidified solution several times. Examination of the resulting sodium carbonate solution by means of a Tyndall beam indicated that no barium ion was carried over.

The sodium carbonate portion was diluted gravimetrically to a volume of 39.00 liters at 25° C with

the appropriate quantity of inert Na_2CO_3 dissolved in water to form a solution that contained all the active carbon as $Na_2C^{14}O_3$, 0.100-M inert Na_2CO_3 as carrier, and free sodium hydroxide to the extent of approximately 0.001 M. The accuracies in weighing the active barium carbonate and in preparing the large volume of solution were each of the order of 0.1 percent. One milliliter of the above solution was therefore equivalent to 2.733 $\pm$0.005 mg of barium carbonate. Analysis by R. A. Paulson, of the Bureau's Chemistry Division, of the original barium carbonate for carbon dioxide indicated a purity of 97.1 percent (with an absolute error of $\pm$0.4 percent), and 1 ml of the solution contained[5] (3.132 $\pm$0.050) $\times 10^{14}$ atoms of C^{14}. Bureau calibrated weights and volumetric glassware were used throughout. Experiments made with A. Schwebel, using an ionization chamber and a vibrating-reed electrometer, demonstrated that 0.1-M sodium carbonate carrier was sufficient to prevent the loss of any significant quantity of active carbonate by adsorption on the walls of the container.

III. Apparatus and Experimental Technique

1. Apparatus

The counter, a sketch of which is shown in figure 1, consists of an outer Pyrex jacket in which are assembled, in order, a 1-in. glass spacer, a disk of aluminum approximately 1 mm in thickness, a copper cathode with a passivated surface, a 1-in. glass spacer, a second disk of aluminum, and finally a 1-in. glass spacer. The outermost spacers are sealed to the glass jacket and prevent movement within the assembly. The aluminum disks define
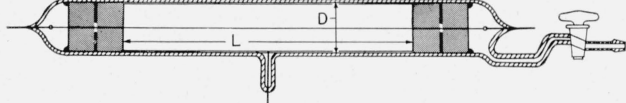
FIGURE 1. *Cross section of carbon dioxide counter showing effective length (L) and diameter (D).*

the active volume of the counter, and a small hole is drilled in each, through which passes a center wire of 3-mil tungsten. The ends of the center wire are sealed to the ends of the outer Pyrex envelope. The inner spacers are identical in length ($\pm$0.01 in.); they serve to insulate the copper cathode from the aluminum disk and to make the ends of the counter identical. It has been shown [4] that the efficiency of these counters is 97 $\pm$1 percent. The number of observed counts per second is, therefore, very nearly equal to the disintegration rate.

A number of experimental counters were built, and a total of six was used for the C^{14} measurements. Their nominal dimensions (inside diameter and length) were 1 in. by 12 in. and 1 in. by 6 in.; $\frac{3}{4}$ in. by 12 in. and $\frac{3}{4}$ by 6 in.; and $\frac{1}{2}$ in. by 12 in. and $\frac{1}{2}$ in. by 6 in. Four measurements of the diameter and two of the length were made of each cathode, and the averages are listed in table 1.

[5] The accuracy in the determination of N, of dN/dt, and of the half-life is given in section V.

TABLE 1. *Dimensions of copper cathodes used in counters*

Counter	Length	Inside diameter	Cathode volume	Difference in cathode volume	Length diameter
	cm	*cm*	*cm³*	*cm³*	
1	29.868 $\pm$0.001	2.357 $\pm$0.004	130.34 $\pm$0.31	----------	12.7
2	15.049 $\pm$0.002	2.351 $\pm$0.001	65.33 $\pm$0.04	65.01 $\pm$0.31	6.4
3	30.162 $\pm$0.002	1.925 $\pm$0.004	87.87 $\pm$0.26	----------	15.7
4	15.079 $\pm$0.010	1.928 $\pm$0.001	44.02 $\pm$0.03	43.85 $\pm$0.27	7.8
5	30.480 $\pm$0.003	1.278 $\pm$0.002	39.10 $\pm$0.08	----------	23.9
6	15.186 $\pm$0.003	1.269 $\pm$0.003	19.21 $\pm$0.06	19.89 $\pm$0.10	12.0

The preparation line (fig. 2) consisted of a 25-ml round-bottomed Pyrex bulb in which the carbon dioxide was generated; a calibrated mixing bulb (146.8$\pm$0.1 ml) equipped with a freeze-out tube, a small flask with a stopcock through which pure CS_2 vapor could be admitted into the mixing bulb, a mercury manometer with a $\frac{1}{2}$-in. bore, and lastly, a pair of counters that could be detached from the system by means of standard-taper glass joints.
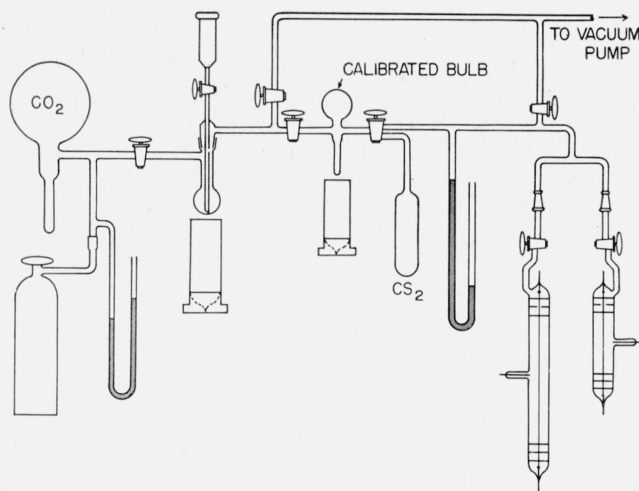

FIGURE 2. *Glass train for preparation of carbon dioxide samples and filling counters.*

The total volume of the system (mixing bulb, counters, manometer, etc.) was readily determined by noting the change in pressure produced by expanding nitrogen gas from the known volume of the mixing bulb (146.8 ml) into the entire system. The total volume ranged from 390 to 650 ml, depending upon the pairs of counters used and could be determined to $\pm$0.2 percent.

The counting system used included a preamplifier and quench circuit of the type used by Mann and Parkinson [5] and a conventional scaler. The resolving time applied to the counter was measured by an oscilloscope and could be varied from 300 to 1,400 microseconds.

2. Experimental Technique

A definite quantity of active sodium carbonate solution (0.5 to 1 ml, measured to $\pm$0.002 ml) was pipetted into the generating flask. The solution was frozen by means of liquid air and the flask evacuated.

The vacuum was shut off, and a large excess (25 to 30 ml) of concentrated sulfuric acid was added slowly and frozen in a layer above the solidified carbonate solution. The liquid air was then removed and the flask allowed to warm to room temperature. The sulfuric acid, because of its lower melting point, was the first to liquefy and, as the carbonate began to melt, the evolution of carbon dioxide proceeded very smoothly. This technique of adding the sulfuric acid served not only to generate the carbon dioxide, but completely to remove the water from it as the reaction progressed. (This technique can also be used with barium carbonate; the barium sulfate is soluble in excess of concentrated sulfuric acid.) The necessity for the quantitative separation of the water from the carbon dioxide, as would have been required had the customary procedure of adding the acid dropwise to the carbonate solution been used, was therefore avoided, and a considerable simplification in the construction of the gas train was rendered possible.

The carbon dioxide was admitted to the calibrated mixing bulb, which contained a pressure of carbon disulfide (approximately 2 cm) requisite for the operation of the counters. The generating bulb was warmed and flushed with a quantity of inactive carbon dioxide that would be sufficient to yield a final pressure between 8 and 15 cm within the counters. The contents of the mixing bulb was frozen by means of liquid air, and any trace of permanent gas removed by pumping. The pump was then shut off, the liquid air removed, and the gases allowed to mix by thermal diffusion, after which the counter assembly and the manometer system were filled. The counters were then removed from the preparation line and placed within a 2-in. lead shield.

3. Correction for Resolving Time

It is well known that the use of CO_2 as a filling gas may result in counters having resolving times as high as 1,000 microseconds and, further, that CO_2+CS_2 counters are not self-quenching. In this respect, such counter fillings are inferior to alcohol-argon, to which is added a small amount of carbon dioxide. The advantage of using the CO_2+CS_2 mixture, on the other hand, is that it eliminates the necessity of working with very small volumes of CO_2 (0.01 to 0.1 ml) and diminishes any concern regarding the possibility of absorbing some of the CO_2 on the comparatively large surfaces of the sample preparation line and on the walls of the counter.

Various equations have been proposed to correct the observed counting rate, C_o, to a "true" one, C_T.

$$C_T = C_o e^{C_T t_r}, \tag{2}$$

$$C_T = C_o(1 + C_o t_r), \tag{3}$$

$$C_T = C_o\left(1 + C_o t_r + \frac{(C_o t_r)^2}{2!} + \frac{(C_o t_r)^3}{3!} + \cdots\right), \tag{4}$$

and

$$C_T = \frac{C_o}{(1 - C_o t_r)}. \tag{5}$$

Equations 2 [6, 7, 8] and 5 [10] have been derived from theoretical considerations. Equations 3 [9] and 4 represent expansions of eq 5 and 2, respectively.

So long as the resolving time, t_r, is small (approximately 300 microseconds), eq 2 to 5 all lead to approximately the same percentage corrections even at fairly high rates of counting, but if the resolving time is of the order of 1,000 microseconds, not all of them are equally suitable. The differences in these equations will be accentuated for high values of t_r and of C_o.

An experimental test of the suitability of eq 2 through 5 was made by observing the counting rate obtained for a mixture of $C^*O_2+CS_2$ as the resolving time applied to the counter was increased systematically. All other variables, including the voltage applied to the counter, were kept constant, and the measurements were made at a point approximately in the center of the plateau. Since C_o is measured experimentally for each setting of t_r, the equation that is the most nearly suitable for obtaining a true counting rate is that which yields calculated values for C_T that show no trend with t_r. The results of such a test are presented in table 2 and in figure 3. Figure 3 shows that eq 2 overcorrects and that eq 3 and 4 undercorrect. Equation 5 appears to be the most suitable, and it was therefore selected for correcting all observed counting rates, C_o, to a true value, C_T. The accuracy in the correction for resolving time is estimated at ± 1 percent.
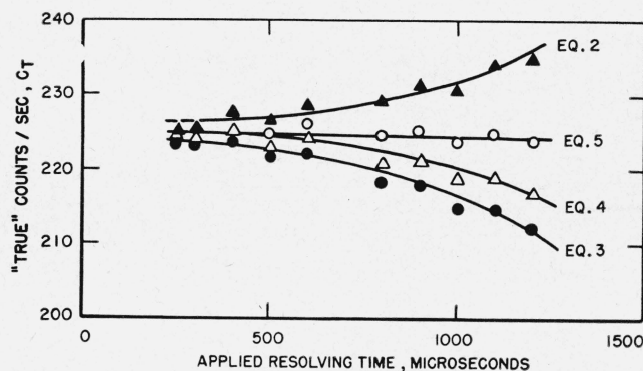

FIGURE 3. *Curves showing the results of application of various resolving time correction formulae to data.*

▲, eq 2; ●, eq 3; △, eq 4; ○, eq 5.

TABLE 2. *Suitability of various equations proposed for correcting observed counting rate, C_o, at a resolving time, t_r*

Applied resolving time	Observed counting rate, C_o	Corrected counting rate obtained by equation			
		2	3	4	5
Microseconds	*Counts/sec*				
350	208.7	225.9	223.4	224.6	225.1
400	206.2	225.6	223.2	223.9	224.7
500	203.5	228.1	224.2	225.3	226.6
600	198.1	227.0	221.7	223.0	224.8
700	195.6	229.0	222.4	224.3	226.0
900	186.7	229.5	218.1	220.9	224.4
1,000	183.9	231.9	217.7	221.0	225.3
1,100	179.4	231.3	214.8	218.5	223.5
1,200	177.1	234.7	214.7	219.0	224.9
1,300	173.2	235.1	212.2	216.8	223.5

4. Effect of Resolving Time on Length of Plateau

The effects of varying the total pressure within the system, the ratio of carbon disulfide to carbon dioxide, the resolving time applied to the counters, etc., were determined. The effect on the plateau of varying the applied resolving time is particularly worthy of mention.

In figure 4 are plotted typical plateaus (for a given mixture of CS_2 and C^*O_2) corresponding to different values of the applied resolving time, t_r. It is evident that longer plateaus are associated with larger values of t_r. As the correction for the effect of the resolving time can be applied by use of eq 5, and a comparatively long plateau is desirable, most of the subsequent experimental work was performed by using $t_r = 1,000$ microseconds, with two measurements being made by using $t_r = 1,400$ microseconds.

A typical plateau obtained by using a resolving time of 1,000 microseconds applied to a pair of counters (1 in. $\times$ 12 in. and 1 in. $\times$ 6 in.) filled with CS_2 and active CO_2 is shown in figure 5. The lowest curve represents the differences in the two counting rates. The flatness of the plateaus indicates that the
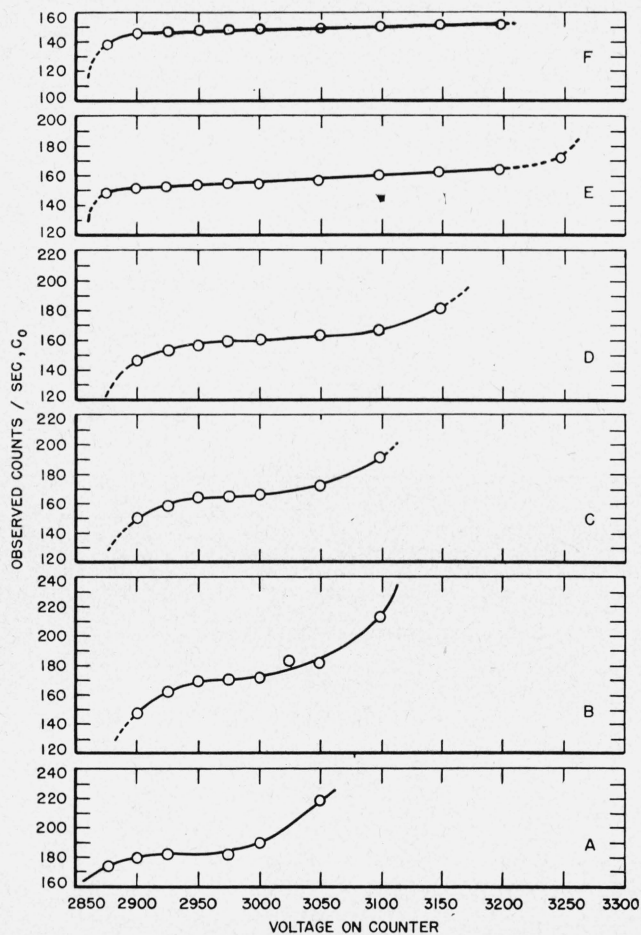

FIGURE 4. *Curves showing the effect of various resolving times on the length of the plateau of the counter.*

A, $t_r = 325$ microseconds; B, $t_r = 600$ microseconds; C, $t_r = 800$ microseconds; D, $t_r = 1,000$ microseconds; E, $t_r = 1,200$ microseconds; F, $t_r = 1,400$ microseconds.
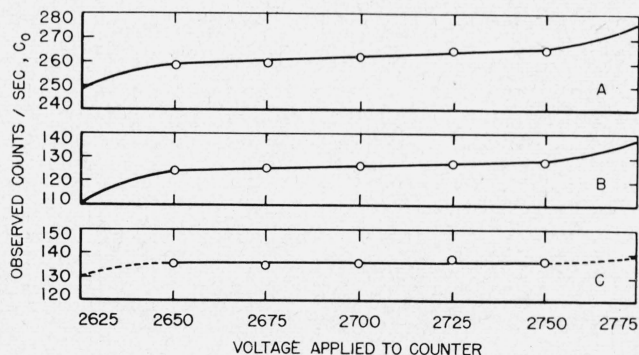

FIGURE 5. *Typical plateau for two sizes of counters with the curve representing the differences in counting rate.*

A, 1 in. by 12 in. counter; B, 1 in. by 6 in. counter; C, difference in counts per second; $t_r = 1,000$ microseconds; $PCS_2 = 2.2$ cm; $PC^*O_2 = 8.6$ cm.

distortion of the electric field of the ends of the counters is small. A counter 1 in. in diameter and 3 in. in length did not give a flat plateau, presumably because the distortion of the field at the ends of the counter amounted to an appreciable fraction of the length of the cathode. Counters whose ratio of length to diameter was 6 or more were found to be satisfactory.

IV. Determination of the Rate of Decay, dN/dt

The rate of decay of the solution containing $Na_2C^{14}O_3$ was measured as follows. The number of counts per second was determined as a function of the applied voltage for each of a pair of counters filled with a definite mixture of CS_2 and active CO_2. Between 100,000 and 200,000 counts were totalized at each voltage setting to obtain a standard deviation ($\sqrt{\text{total counts}}$) between 0.3 and 0.2 percent. Corrections were then applied to each point for the resolving time (eq 5) and for the background to yield a net counting rate, C_n. The difference in C_n for the long and short counters were averaged. The activity of the solution in disintegrations per second per milliliter was calculated from

$$(\text{dis/sec})/\text{ml} = \frac{\Delta C_n \times V}{\Delta V \times \text{ml} \times 0.97}, \qquad (6)$$

where ΔC_n is the average difference in net counting rate for the pair of counters used, ΔV is the difference in their cathode volumes (table 1), V is the total volume of the system, ml is the number of milliliters of the active solution taken, and 0.97 is the efficiency [4] of the counting system.

In table 3 is presented a condensation of the data that were obtained. In columns 1, 2, 3, 4, 5, and 6 are shown, respectively, the nominal dimensions of the pairs of counters used, the differences in their cathode volumes, the volume of active Na_2CO_3 solution taken, the applied resolving time in microseconds, the total volume of the system, and the average net difference in counting rate. In column 7 is computed the activity of the carbonate solution in disintegrations per second per milliliter. The aver-

age value is 1,280 (dis/sec)/ml with a probable error of the mean $\left(E=\dfrac{0.845\,\Sigma\,d}{n\sqrt{n-1}}\right)$ or ± 8 (dis/sec)/ml.

TABLE 3. *Condensation of data obtained for the activity of a solution of Na_2CO_3 containing C^{14}*

Counter	Difference in cathode volume	Volume of Na_2CO_3 taken	Applied t_r	Total volume of system	Average net difference in rate	Activity of solution
in.	*ml*	*ml*	μ *seconds*	*ml*	*Counts/ sec*	*dis/sec/ ml*
1 by 12 and 1 by 6	65.01	0.502	1,000	637.9	63.7	1,284
1 by 12 and 1 by 6	65.01	1.013	1,000	620.4	135.9	1,320
1 by 12 and 1 by 6	65.01	0.388	1,000	639.5	49.9	1,304
1 by 12 and 1 by 6	65.01	1.013	1,400	637.8	130.3	1,300
¾ by 12 and ¾ by 6	43.85	1.013	1,000	559.4	96.9	1,258
¾ by 12 and ¾ by 6	43.85	1.013	1,400	538.3	102.6	1,282
½ by 12 and ½ by 6	19.89	1.013	1,000	394.5	60.5	1,221
½ by 12 and ½ by 6	19.89	1.013	1,000	391.5	63.5	1,272
Average						1,280
$\left(E=\dfrac{0.845\,\Sigma\,d}{n\sqrt{n-1}}\right)$, probable error						± 8

V. Sources of Error

The accuracy in the determination of the half-life of radiocarbon can be estimated as follows. The accuracies in the determination of N involve ($\pm 0.04/3.876$) or ± 1.0 percent in the isotopic ratio, ± 0.1 percent each in the weighing of the barium carbonate and in preparation of the solution, and ± 0.4 percent in the analysis of the barium carbonate. The accuracy [6] in N is therefore ± 1.6 percent.

The accuracy in dN/dt involves the error in the gas counting ($\pm 8/1280$) or ± 0.6 percent; in the determination of the total volume of the counting system, ± 0.2 percent; in the application of the correction for the resolving time, ± 1.0 percent; and for the efficiency of the counting system, ± 1.0 percent. The accuracy in dN/dt is therefore ± 2.8 percent. The combination of ± 1.6 percent in N and of ± 2.8 percent in dN/dt corresponds to an accuracy of ± 4.4 percent in the half-life of radiocarbon.

VI. Calculation of the Half-Life of C^{14}

The half-life of C^{14} was computed according to eq 1. N has been previously calculated to be 3.132×10^{14} atoms of C^{14}/ml of solution, and dN/dt from table 3 is 1,280 dis/sec/ml. The half-life of C^{14} is therefore 5,370 ± 200 years.

VII. Comparison With Other Determinations

The half-life obtained here, 5,370 ± 200 years, is in fair agreement with that obtained by Jones [2] (5,589 ± 75 years) and by Libby [1] (5,580 ± 45 years), but differs from that reported by Mann and coworkers [12] (6,360 ± 200 years) and by Yaffe and Grunlund [13] (7,200 ± 500 years). A summary of the values for the half-life is presented in table 4.

[6] The accuracy is $|a_1|+|a_2|+ \ldots |a_n|$, where $|a|$ represents the numerical value of the accuracy without regard to sign.

TABLE 4. *Comparison of values obtained for the half-life of C^{14}*

Year	Reference	Authors	Method used for determination of—		$T_{\frac{1}{2}}$
			Isotopic ratio	Activity	
					Years
1946	[14]	Reid, Dunning, Weinhouse, Grosse	Mass spectrometer (1.71% of C^{14})	End-window	4,700 $\pm$(235 to 470)
1948	[15]	Norris and Inghram	Mass spectrometer (3.23 and 3.35% of C^{14}).	do	5,100 ± 200
1948	[13]	Yaffe and Grunlund	Mass spectrometer (6.21% of C^{14})	do	7,200 ± 500
1949	[12]	Hawkins, Hunter, Mann, Stevens	do	$C^*O_2+CS_2$	6,360 ± 200
1949	[1]	Engelkemeir, Hamill, Inghram, Libby.	Mass spectrometer (1.28 to 6.14% of C^{14}).	C^*O_2+alcohol-argon	5,580 ± 45
1949	[2]	Jones	Mass spectrometer (39.4% of C^{14})	do	5,589 ± 75
1950	This paper	Manov and Curtiss	Mass spectrometer (3.876% of C^{14})	$C^*O_2+CS_2$	5,370 ± 200

The measurements of Libby and of Jones were performed by using single counters in which the major constituent of the filling was alcohol-argon, with the carbon dioxide introduced in a small quantity. End effects were determined for counters of various sizes, and corrections were applied to the data, and the assumption was made that alcohol-argon-$C^{14}O_2$ counters were 100-percent efficient.

The value for the half-life of radiocarbon would be decreased if the barium carbonate were not entirely pure, or if the gas counters were not 100-percent efficient. Adsorption of a small amount of CO_2 on the walls of the glass system prior to entering the counter would tend to increase the value obtained for the half-life.

The value found by Yaffe and Grunlund was obtained by using an aliquot of the same Na_2CO_3 solution as used by Hawkings, Hunter, Mann, and Stevens, except that the counting was performed by using barium carbonate and an end-window counter.

VIII. Summary

The isotopic ratio of C^{14} in a mixture of inert and radioactive $BaCO_3$ was determined by a mass-spectrometric analysis of the carbon dioxide prepared therefrom. A known quantity of this barium carbonate was used to prepare a solution containing active Na_2CO_3, the activity of which was determined by using internal Geiger-Müller counters. The value for the half-life of C^{14} was found to be 5,370 ± 200 years.

IX. References

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