

Enrichment of Radiocarbon for Dating Samples up to 75,000 Years

P. M. Grootes, W. G. Mook, J. C. Vogel *

Physics Laboratory, State University Groningen

A. E. de Vries, A. Haring, and J. Kistemaker

F. O. M. Institute for Atomic and Molecular Physics, Amsterdam

(Z. Naturforsch. 30 a, 1–14 [1975]; received September 2, 1974)

The range of the radiocarbon dating method can be extended by about 20,000 years by means of thermal diffusion isotopic enrichment. A description of the Clusius-Dickel type enrichment columns and their operation is given. Prior to enrichment the carbonaceous sample material is combusted to CO_2 and then reduced to CO. The enriched sample is re-oxidized to CO_2 . The combustion-, reduction- and oxidation-apparatus and their operation are described.

The performance of the thermal diffusion columns has been tested and an empirical, volume independent relation between the isotope separation factors of $^{14}\text{C}^{16}\text{O}$ and all molecules with mass $\langle 30 \rangle$ is given

$$q^{14} - 1 = (1.13 \pm 0.05) (q^{30} - 1) + (0.035 \pm 0.005) (q^{30} - 1)^2.$$

The influence of contaminations on the reliability of ^{14}C dates obtained with this method is discussed. Laboratory contaminations can be kept below the detection limit as is shown by the preparation of two anthracite samples. Still there may be some influence on dates obtained for very old samples. As far as laboratory contaminations are concerned, dates up to 75,000 years can be obtained.

Introduction

Age determination by means of natural radiocarbon today plays an important role in Archeology and Quaternary Geology. Although increasing attention is paid to other dating methods such as thermoluminescence¹, obsidian hydration² and potassium-argon³, the accuracy and the absolute character of the radiocarbon method could not yet be equaled.

The radiocarbon technique in itself carries certain limitations, however. The most serious is the rather short half life of ^{14}C , on a geologic time scale (according to ^{14}C convention 5568 years is used; a more recent value⁴ is 5730 ± 40 calendar years). Since the development of the radiocarbon dating method⁵ much energy has been spent on extending the range of the method.

The upper age limit is determined by the background of the counters. The standard deviation of the background counting rate (in a given counter in a given time) determines the lowest radio-activity which is still clearly distinguishable from statistical fluctuations in this background (2σ criterion giving $\cong 98\%$ probability), and thus the maximum age. For the most sensitive counter set-ups presently in use the range of the radiocarbon dating method in

a 48 hours counting period extends back to approximately 50,000 years.

This time-range spans the whole known history of modern man and also a substantial part of the last glaciation. It is, however, of interest to be able to date events in the earlier part of the last glaciation and the middle-palaeolithic, which still is well below the lower age limit of the potassium-argon dating method. In order to accomplish this, special counters can be constructed, having a high figure of merit $F = A_0/\sqrt{B}$, where A_0 is the activity of the recent standard CO_2 and B the background of the counter measured with a CO_2 filling with an amount of ^{14}C well below the detection limit. Also with a prolonged count a few half lives can be gained. The range becomes then some 60,000 years⁶.

A different approach was chosen by De Vries who obtained a more than tenfold increase in the specific activity of a sample by isotopic enrichment of carbon monoxide in Clusius-Dickel thermal diffusion columns, thus extending the range of the radiocarbon method by about 20,000 years. The enrichment apparatus was developed at the F.O.M. Institute of Atomic and Molecular Physics in Amsterdam^{7,8} in 1957. During 1970 the essential part of the apparatus was moved to the Groningen Radiocarbon Laboratory and has been used since then with some modifications.

* Present address: N.P.R.L., C.S.I.R., Pretoria.

Reprint requests to Physics Laboratory, University of Groningen, Westersingel 34, Groningen, The Netherlands.



Presently an apparatus for the thermal diffusion enrichment of methane for radiocarbon dating is being put in operation in Munich by Kretner⁹. The performance of this apparatus is comparable with that of the CO enrichment set-up described in this article (compare: 7.5 l NTP of methane gas enriched by a factor 8 in 24 days and by a factor 11.4 in 45 days using 120 g of carbon and 6.3 l NTP of CO gas enriched by a factor 11.4 in 40 and 12.8 in 44 days using 130 g of carbon). Further, an enrichment apparatus is being constructed in Kiel by Erlenkeuser¹⁰ for methane and in Seattle for CO¹¹.

It is the aim of this article to give a description of the enrichment apparatus and its performance and of the laboratory contamination problem, which becomes important at these extremely low sample activities. Some results will be given, but the majority of the dates obtained so far will be published and discussed elsewhere.

Thermal Diffusion

The theory of the thermal diffusion effect and of the thermal diffusion column has been treated and reviewed by many authors¹²⁻¹⁷.

The thermal diffusion effect strongly depends on the shape of the intermolecular potential. For molecules with a repulsive potential proportional to $r^{-\nu}$ (r is the distance between molecules and $\nu > 5$) placed in a temperature gradient, it generally causes the heavy molecules to accumulate at the cold outer — and the light ones at the hot inner wall. The simple rigid elastic-sphere model corresponds to $\nu = \infty$ and gives the largest thermal diffusion effect. Depending on how the actual behaviour of the molecules resembles that of rigid elastic spheres (hardness = 1), a certain hardness from 0 to 1 can be ascribed to them.

In a thermal diffusion column the horizontal temperature gradient effects a small isotope separation. The convection current running down along the cold and up along the hot wall, results generally in a net transport of the heavy isotope down the column and of the light isotope to the top. By flushing the column at the top with fresh gas, a considerable enrichment in the heavy isotope can be obtained for the gas at the bottom of the column. An enriched gas sample can be collected by connecting a suitable volume to the bottom end and closing it off when the desired enrichment has been reached.

Since the performance of a thermal diffusion column is determined by several parameters of which the effects are not accurately known, a theoretical calculation of the resulting enrichment after a given time has a rather limited accuracy. Thus the isotopic enrichment obtained should be determined mass-spectrometrically for each sample.

When considering the enrichment of a certain isotope by thermal diffusion in the gas phase, one should choose a light molecule containing the isotope (large relative mass difference between the isotopic molecules) that is “hard”, relatively easy to make and that readily offers the possibility of measuring the enrichment. For carbon the most suitable molecules are CH₄ and CO. Radiocarbon samples are initially always combusted to CO₂ that is either used directly as a counting gas, or subsequently converted to methane, acetylene or benzene and counted in this form. The molecule CO has been chosen for the enrichment since firstly the reduction of CO₂ to CO is relatively simple and secondly, the greater thermal stability and hardness of CO as compared to CH₄ compensate for the effect of smaller relative mass difference. Finally, the isobaric molecule ¹²C¹⁸O offers a possibility of indirectly measuring the ¹⁴C enrichment mass-spectrometrically.

Gain in Age

In this article we will use the usual definition of the separation factor^{15, 17}

$$q \equiv \frac{\text{isotope ratio in enrichment volume}}{\text{isotope ratio in reservoir}}$$

while we define the more practical enrichment factor as

$$q' \equiv \frac{\text{concentration obtained by enrichment}}{\text{concentration prior to enrichment}}$$

An enrichment with a factor $q^{14'} = 2^n$ gives a gain in datable age of n half-lives. The actual ¹⁴C enrichment is established by mass-spectrometrically measuring the mass $\langle 30 \rangle$ enrichment $q^{30'}$ (virtually due to ¹²C¹⁸O), calculating the corresponding isotope separation factor q^{30} and using a calibration curve for the relation between the ¹⁴C and $\langle 30 \rangle$ separation factors.

If we denote the measured activity of the enriched sample by A_e and the sample activity without enrichment by A , then we have

$$A_e = A q^{14'} \quad (1)$$

with $A = A_0 e^{-\lambda t}$ ($1/\lambda = \frac{t_{1/2}}{\ln 2} = 8033$) we then have for the age of the sample,

$$T = -1/\lambda (\ln[A_e/A_0] - \ln q^{14'}) \quad (2)$$

where $t_{1/2}$ is the conventional ^{14}C half-life (5568 the activity of NBS oxalic acid) and T is the ^{14}C age of the sample. The gain in age thus is $\ln q^{14'}/\lambda$, which means 18,500 years for a ^{14}C enrichment $q^{14'} = 10$.

The gain in dating range is accompanied by an additional uncertainty due to the determination of the $\langle 30 \rangle$ enrichment $q^{30'}$ and the calibration relation.

For the standard deviation in the sample activity A we find from (1)

$$\sigma_A = \{(\sigma_{A_e}/q^{14'})^2 + [-A_e \sigma_{q^{14'}}/(q^{14'})^2]^2\}^{1/2}. \quad (3)$$

For samples with a low specific activity (A_e corresponding to a ^{14}C age $> 40,000$ years) this leads to an asymmetrical standard deviation for the measured age:

$$\pm \sigma_T = -1/\lambda \ln[1 \mp \{(\sigma_{A_e}/A_e)^2 + (\sigma_{q^{14'}}/q^{14'})^2\}^{1/2}] \quad (4)$$

as can easily be seen from a series expansion.

The first term is the normal standard deviation due to the statistical character of the counting process. The other one mainly represents the uncertainty in the determination of the mass $\langle 30 \rangle$ enrichment. As will be discussed later the relative accuracy for $q^{14'}$ is approximately 2%.

For recent samples, where σ_{A_e}/A_e is small, this means, that the enrichment introduces a sizeable extra uncertainty in the age determination. For very old samples this can be neglected. If our criterion is an accuracy in σ_A of 10%, we can neglect the contribution of the enrichment to the standard deviation for the counter used, in a two days counting period for $A_e < 0.0218 A_0$ ($T > 31,000$ years), and in a four days counting period for $A_e < 0.0154 A_0$ ($T > 33,500$ years). Thus, under the present circumstances the inaccuracy with which the enrichment is known does not influence the age-determination of very old samples ($T > 60,000$ years).

For an enriched sample the counting statistics are better ($\sigma_{A_e}/A_e < \sigma_A/A$), whereas at the same time an extra uncertainty $\sigma_{q^{14'}}/q^{14'}$ is introduced. Consequently, a gain in accuracy can be obtained by en-

richment under certain conditions. If we compare a 30 days enrichment procedure (reduction and oxidation included) resulting in an enrichment $q^{14'} = 8$, in combination with a two days counting period with a 32 days counting period for the original sample, the accuracy has been increased by enrichment for samples having an activity $A < 0.0088 A_0$ or $T > 38,000$ years. If, instead, for the normal sample a two days counting period is taken, the accuracy is already better for samples having an activity of $A < 0.06 A_0$ ($T > 23,000$ years).

However, the amount of work involved in an enrichment dating makes it unattractive to pursue a better accuracy in this way.

Apparatus

The Thermal Diffusion Columns

The thermal diffusion columns used are of the Clusius-Dickel type and consist of a 3 m pyrex glass tube having a diameter of 8.9 to 9.9 mm, the larger diameter at the top, with a 0.3 mm diameter Platinum-Iridium (80%–20%) wire suspended in the centre. The wire is centered by triangular spacers (Pt–Ir 80–20; 0.1 mm thick), that have been soldered to the wire with gold at regular distances of approximately 25 cm. The wall of the pyrex tube is cooled from the outside by water flowing from bottom to top between this wall and a second concentric pyrex tube of $\cong 30$ mm diameter (Figure 1). The complete enrichment apparatus consists of 18 columns; 2 in series on top of each other and 9 of these double columns in parallel. The double columns are interconnected at the top (Fig. 2) and each has a 0.55 l sample bulb at the bottom. Through the top of the columns gas from any combination of 4 large storage bulbs of pyrex glass (volumes resp. 50 l, 80 l, 111 l and 111 l) can be circulated thermally.

Prior to enrichment the wires are heated up to 500–600 °C in an oxygen atmosphere in order to remove traces of carbon which may have been deposited on the wires. Then the columns are pumped to a vacuum of $\cong 10^{-5}$ torr. Before filling, the columns are washed three times with approximately 1 l of the CO sample to be enriched. The whole system is then filled with CO to a pressure of about 900 torr. Samples of the gas prior to enrichment are taken from the top and the bottom of the columns. The power consumption during enrichment is some 3.5 kW (6 A at 190 V for each group of 3 double columns, fed from one power supply) giv-

ing a wire temperature of $\cong 650^{\circ}\text{C}$ (faintly red) while the cold wall temperature is $20 - 25^{\circ}\text{C}$. The apparatus is safeguarded against water leakage and overheating and against vacuum breakdown during pumping.

Using a storage volume of about 200 l, an isotopic enrichment in ^{14}C by a factor of 10 can be reached in about four weeks.

The Combustion System

The standard procedure for the conversion of carbonaceous material to pure CO_2 has been described earlier¹⁸⁻²⁰ (Figure 3). Modifications are:

(i) the use of high purity gases * for the combustion, making alkali wash bottles superfluous; (ii) additional purification of these gases from moisture and hydrocarbons by passing them through two traps at dry-ice temperature prior to combustion; (iii) the heating of the sample material at 1000°C by means of an electrical furnace with automatic transport; (iiii) omission of the Radon purification. This can be done, since the time between the combustion and completion of the enrichment procedure (30 days) is long compared with the Radon half-life (3.8 days) and ensures a sufficient decay. The sample is stored after combustion in a 1 l CO_2 cylinder.

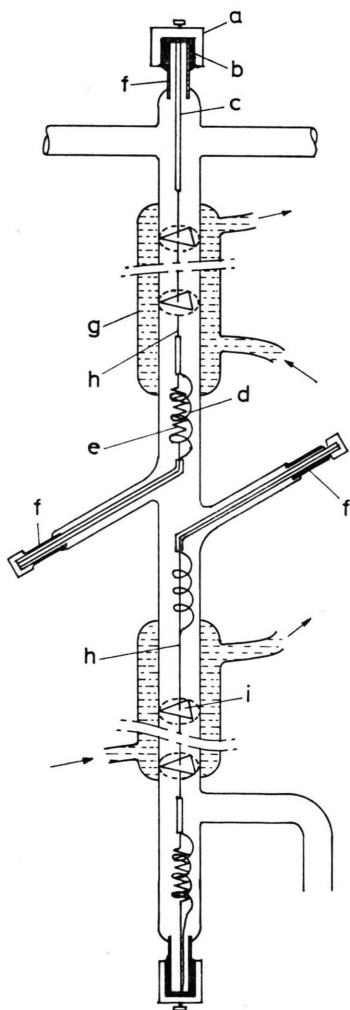


Fig. 1.

Fig. 1. Construction thermal diffusion column. a — copper cap, b — tin solder, c — copper capillary, d — flexible copper wire, e — steel spring, f — kovar, g — pyrex glass diffusion column with cooling jacket, h — Pt-Ir (80%–20%) wire, i — Pt-Ir (80%–20%) triangle ("spacer").

Fig. 2. Thermal diffusion system, a — storage volume V_- , b — thermal diffusion columns, c — enriched sample volume V_+ , d — thermal circulation, e — sampling point, f — mercury manometer, g — Pirani gauge, h — Penning highvacuum gauge

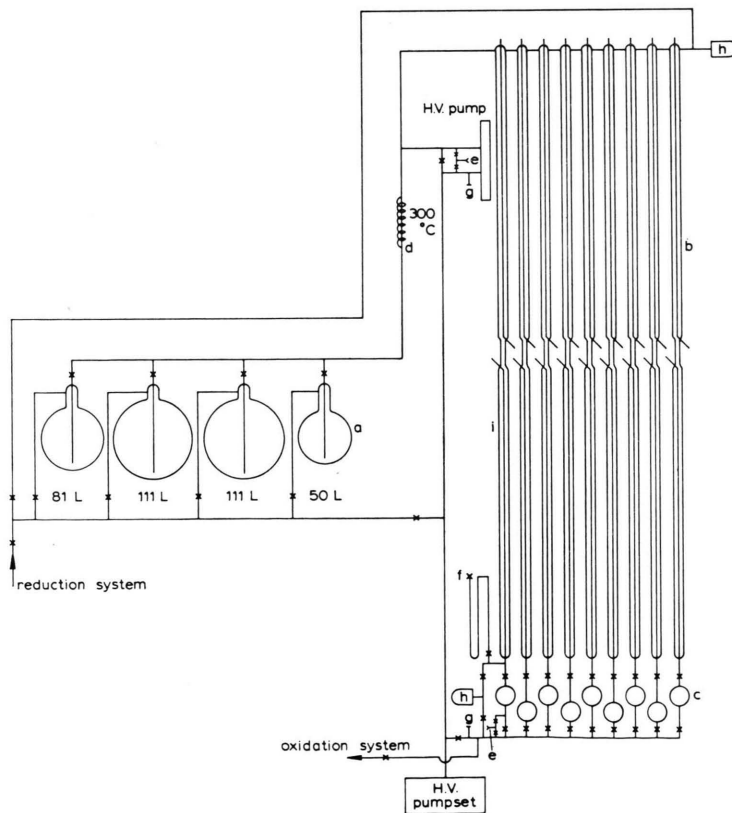


Fig. 2.

The Reduction System

The CO₂ sample is reduced to CO by passing it from the cylinder via a pressure regulator through a zinc-asbestos mixture (10 : 1 by weight, \cong 1.5 kg) heated to about 420 °C in a temperature controlled furnace (Figure 4). The asbestos, which serves to facilitate the gasflow through the reduction furnace is heated before use at 900 °C in air to remove possible organic contaminations and water. Then it is

mixed with the zinc which has been washed with di-ethyl ether to remove adhering grease, and the mixture is thoroughly degassed by prolonged pumping at 125 °C. At higher temperatures the reduction is speeded up, but the melting of the zinc (at 419.4 °C) and the softening of the glass tube limit the temperature to be used. The zinc-asbestos at 420 °C and the system are flooded three times with about 100 ml NTP of CO₂ from the cylinder and

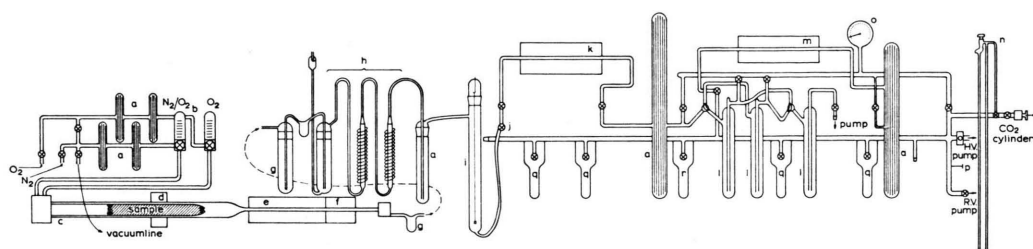


Fig. 3. Combustion system. a — drying traps at -80°C , b — flowmeter with needle valve, c — combustion tube (quartz), d — combustion furnace at 1000°C , e — CuO furnace at 800°C , f — Ag furnace at 500°C , g — water trap, h — KMnO₄ wash bottles, i — Cottrell electrostatic dust collector, j — needle valve, k — Ag furnace at 450°C , l — CO₂ traps at liquid air temperature, m — Cu and Ag furnace at 450°C , n — mercury manometer, o — Bourdon manometer, p — Pirani gauge, q — storage bulbs 10 L, r — storage bulb 20 L.

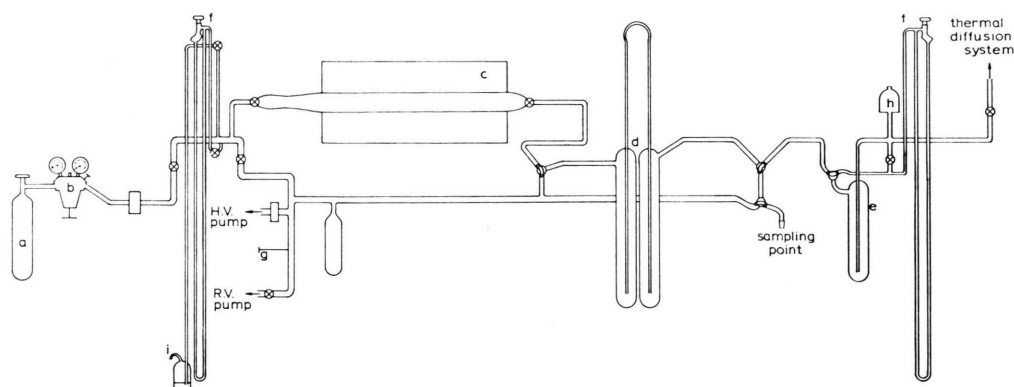


Fig. 4. Reduction system. a — CO₂ cylinder, b — pressure regulator, c — zinc-asbestos furnace at 420°C , d — CO trap at -195°C , e — CO₂ trap at liquid air temperature, f — mercury manometer, g — Pirani gauge, h — Penning highvacuum gauge, i — overpressure protection.

* L'Air Liquide N.V. high purity gases. Nitrogen A 28 ($\text{H}_2\text{O} \leq 5 \text{ vpm}$; $\text{N}_2 + \text{noble gases } 99.999\%$) Oxygen A 40 ($\text{H}_2\text{O} \leq 5 \text{ vpm}$; $\text{C}_n\text{H}_m \leq 5 \text{ vpm}$; $\text{O}_2 \text{ } 99.99\%$).

pumped, before starting the reduction of the bulk of the sample. At a pressure drop across the zinc-asbestos of some 400 torr the speed of reduction is approximately 10 l/h and virtually no CO_2 passes the furnace ($<0.1\%$). Over 60% of the zinc in the furnace can be oxidized to ZnO in this way. In order to keep pressures moderate, trap any CO_2 and have the possibility of filling the columns to any desired pressure, the CO gas is passed through a double trap at liquid nitrogen temperature (-195.8°C) where the CO condenses to a colourless clear liquid with a vapor pressure of about 470 torr. When the reduction has been completed, the CO is evaporated and led into the columns through a trap at liquid air temperature to condense any CO_2 present.

The Oxidation System

Since the enriched sample has to be counted in the same way as normal samples, it has to be re-oxidized to CO_2 . The enriched gas in the 9 sample bulbs at the bottom is closed off from the columns and admitted to the oxidation system (Figure 5). There it is expanded into a 10 l bulb. After closing this bulb the residual gas ($\cong 30\%$) is quantitatively adsorbed in 40 g of fine grained silicagel at liquid-air temperature (residual pressure $<5 \cdot 10^{-3}$ torr). The silica should be pretreated with hot HNO_3 and washed thoroughly thereafter to remove radio-active impurities (Uranium) that produce Radon. The

silicagel has first been evacuated overnight at about 200°C . The adsorbed gas is desorbed by heating the silicagel to about 200°C and led into the 10 l bulb. From this enriched gas mixture a sample is taken to measure the enrichment that has been obtained.

The gas is oxidized by passing it through a CuO furnace at 450°C and condensing the CO_2 formed in a trap at liquid-air temperature. Although some CO passes the furnace, reduction can be made quantitative by adsorbing this CO in the silicagel and desorbing it again for circulation through the CuO furnace. After recycling twice, the pressure in the system remains constant indicating that the oxidation is complete. Some non-condensable gases can be pumped off ($<0.03\%$ of the initial amount of gas) after which the enriched CO_2 sample is transferred to a storage bulb. The total procedure takes about 10 hours. After each oxidation the CuO furnace has to be regenerated by heating it at 450°C in oxygen.

Counter

The radio-activity of the samples is measured in a proportional CO_2 counter as designed by Vogel²⁰, having an effective volume of 1.7 l. Filled to a pressure of 2063 torr the background is presently 1.95 ± 0.01 cpm and the recent count is 30.81 cpm giving a figure of merit of 22.0. The maximum measurable age in a two days count is 51,000 years (2σ criterion).

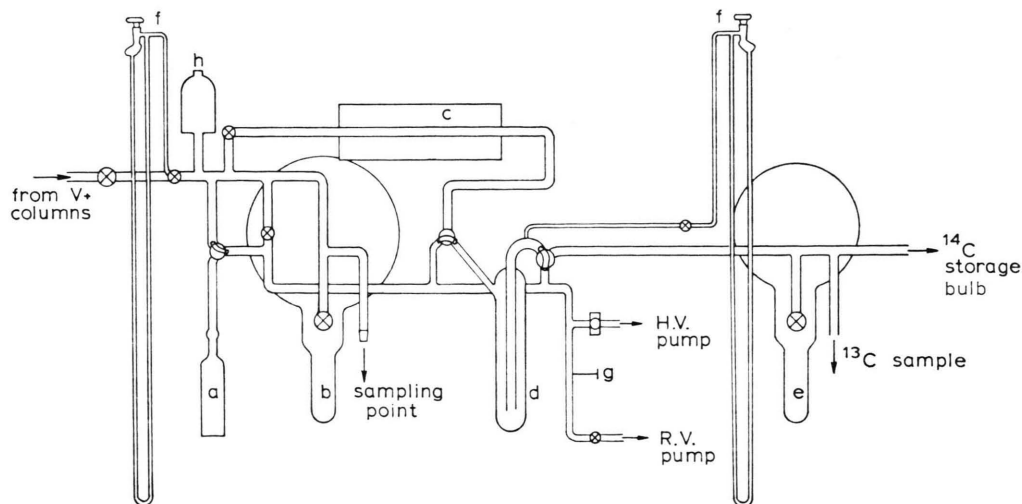


Fig. 5. Oxidation system. a — silica adsorber, b — 10 L storage bulb, c — CuO furnace at 450°C , d — CO_2 trap at liquid air temperature, e — 6.5 L calibration volume, f — mercury manometer, g — Pirani gauge, h — Penning highvacuum gauge.

Mass spectrometer

The isotopic composition of the gas samples before and after enrichment is measured with a Varian M86 dual collector mass spectrometer. The interpretation of the measurements for CO_2 has been treated earlier²¹. The testing of the behaviour of the columns during the enrichment is also done mass-spectrometrically.

Experiments and Discussion*Thermal diffusion*

The thermal diffusion apparatus has been designed specifically for the production of enriched CO for radiocarbon dating. Although CO is the simplest gaseous molecule available, a sample of natural CO still is a rather complex mixture of 9 isotopic molecules (Table 1) in which the concen-

Table 1. Composition of CO from natural recent CO_2 .

Mass	Molecule	Concentration
<28>	$^{12}\text{C}^{16}\text{O}$	0.9868
<29>	$^{13}\text{C}^{16}\text{O}$	0.01085
	$^{12}\text{C}^{17}\text{O}$	0.0037
<30>	$^{12}\text{C}^{18}\text{O}$	0.00200
	$^{13}\text{C}^{17}\text{O}$	$4.1 \cdot 10^{-6}$
	$^{14}\text{C}^{16}\text{O}$	$\approx 10^{-12}$
<31>	$^{13}\text{C}^{18}\text{O}$	$2.2 \cdot 10^{-6}$
	$^{14}\text{C}^{17}\text{O}$	$\approx 4 \cdot 10^{-16}$
<32>	$^{14}\text{C}^{18}\text{O}$	$\approx 2 \cdot 10^{-15}$

tration of the ^{14}C containing molecular species, prior to enrichment, is not measurable. On the other hand, a theoretical calculation of the ^{14}C enrichment has only a limited accuracy due to the complexity of the gas mixture and the many parameters influencing the thermal diffusion process i.e. temperature of wire and cold wall, pressure, excentricity of the wire, etc. Thus a calibration is required.

We will first give measurements on the behaviour of (i) the different individual columns and (ii) one column as a function of time. The measurements were made by mass-spectrometric analysis of the <29>/<28> and <30>/<28> ratios in CO. Further, the relation between the ^{14}C enrichment of a sample and that of its stable isotopes is given for two series of measurements. In Groningen CO_2 from recent shells was used, in Amsterdam a mixture of CO_2 from anthracite and recent wood respectively oxalic acid.

Individual column performance

On 6 occasions a sample has been taken from the positive (heavy isotopes) storage volume of each column separately after completion of the enrichment. The enrichment of each sample relative to the original gas, q' , was calculated from the mass-spectrometric measurements.

Corrections were made for a decrease in concentration in the enriched gas of the abundant isotopic molecule <28> and for the collection of ions of different mass by the B collector of the mass spectrometer (masses <28> to <31>; c.f. Reference 21). The average enrichment time was 34 days (minimum 21 days and maximum 44), giving an average enrichment of $q^{29'} = 4.7$ and $q^{30'} = 8.4$ (minimum 3.8 resp. 6.7 and maximum 5.0 resp. 9.8). Then the performance of each column separately was calculated relative to the mean enrichment of all columns for each enrichment procedure for both mass <29> and <30>.

The average column performances after 6 enrichments are given with their standard deviation for each column in Figure 6. The values range from

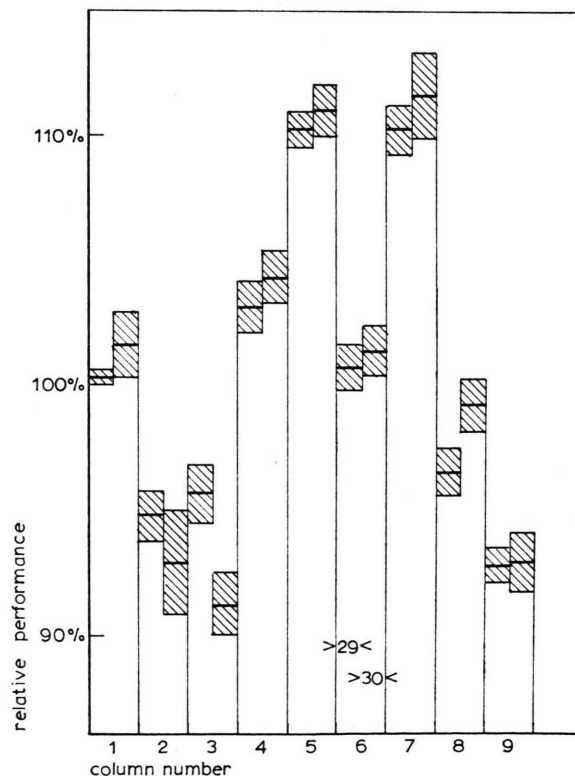


Fig. 6. Enrichment in the individual columns relative to the average enrichment of all columns.

91%±1% to 111%±1.5%, indicating the importance of small differences between “identical” columns. This also demonstrates the dubious value of a theoretical calculation of the enrichment in a Clusius-Dickel thermal diffusion column.

*The gas composition as a function of time
for one column*

The isotope separation takes place in a system with a positive volume V_+ and a column volume V_c that are approximately equal and much smaller than the “negative” storage volume V_- . During enrichment, normally no gas is drawn from the columns. From the column under investigation (number 1) the minimum amount necessary for a mass-spectrometric analysis was taken (3 ml i.e. 0.5% of the total amount of gas in V_+ of one column). From the mass-spectrometric measurements the isotopic enrichment factor $q^{30'}$ can be calculated using the corrections mentioned in the preceding section.

Assuming the disturbance introduced by the sample extraction to be small, the results obtained give the enrichment of column 1 as a function of time (Figure 7).

Since the storage volume V_- is finite, an enrichment of certain isotopes in the columns and V_+ corresponds to a decrease in concentration of these

isotopes in V_- . Thus the thermal diffusion isotope separation factor q is related to the isotopic enrichment q' by

$$q^{v'} = q' \cdot \frac{C_{V_-}^{v*}}{C_0^v} \cdot \frac{C_{V_+}^{28*}}{C_{V_-}^{28*}} \quad (5)$$

where C^v is the concentration of the heavy isotopic CO molecules (v referring to mass 29 or 30), while the indices \dots_0 and \dots^* respectively refer to the gas before and after enrichment. Here the change in concentration of the common isotopic molecule leads to

$$C_{V_+}^{28*} / C_{V_-}^{28*} = \frac{1 - q^{29'} C_0^{29} - q^{30'} C_0^{30}}{1 - C_{V_-}^{29*} - C_{V_-}^{30*}}$$

and the finite storage volume V_- to

$$C_{V_-}^{v*} = \frac{C_0^v \{V_- - V_c (\frac{1}{2} q^{v'} - 1) - V_+ (q^{v'} - 1)\}}{V_-}$$

It is assumed, that the gas in V_+ is uniform in composition and enriched by the factor q' , while the temperature and pressure of the gas in V_+ and V_- are equal. For the column gas it is difficult to calculate the average enrichment and temperature exactly. Reasonable agreement between the calculated and the actual decrease in concentration in V_- is obtained (Fig. 8b) if for the average enrichment of the column gas an empirical value of $\frac{1}{2} q'$ is

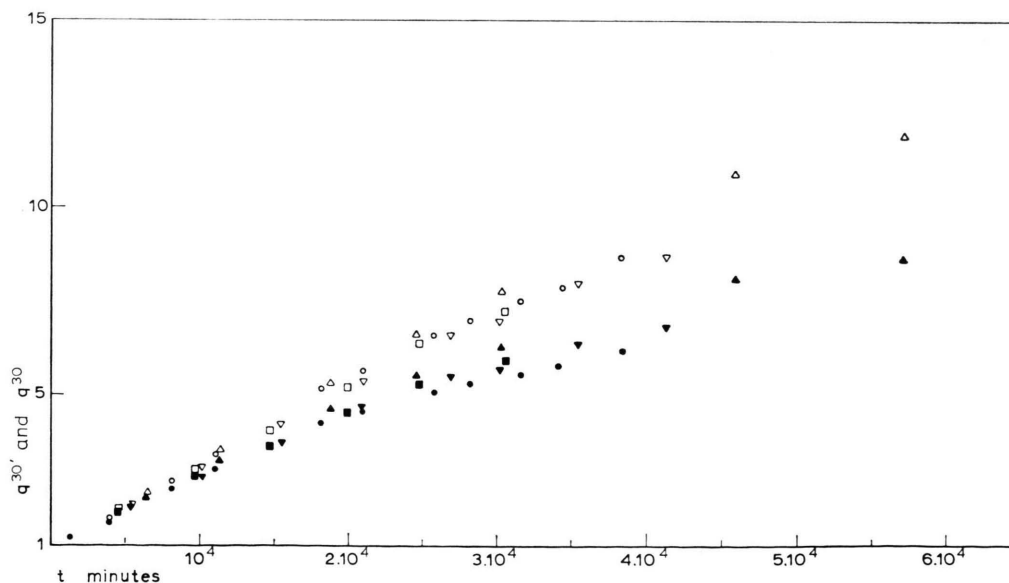


Fig. 7. Enrichment and isotope separation as a function of time for column 1. $\circ q^{30}$ and $\bullet q^{30'}$ -cylinder gas, $V_- = 140$ l, $p = 91$ cm, 250 W thermal circulation; ∇q^{30} and $\blacktriangledown q^{30'}$ -recent shells I, $V_- = 231$ l, $p = 91$ cm, 250 W thermal circulation; $\circ q^{30}$ and $\blacksquare q^{30'}$ -recent shells V, $V_- = 231$ l, $p = 92$ cm, 250 W thermal circulation; $\triangle q^{30}$ and $\blacktriangle q^{30'}$ -anthracite I, $V_- = 202$ l, $p = 91$ cm, 500 W thermal circulation.

taken without paying attention to temperature. The relation $(q'' - 1)C_{V-}^*/\ln q''$ for the average composition of the gas in the columns²² can not be used, since this applies to columns under equilibrium conditions, while in our case the columns are operating in a transient state in the beginning of the separation process.

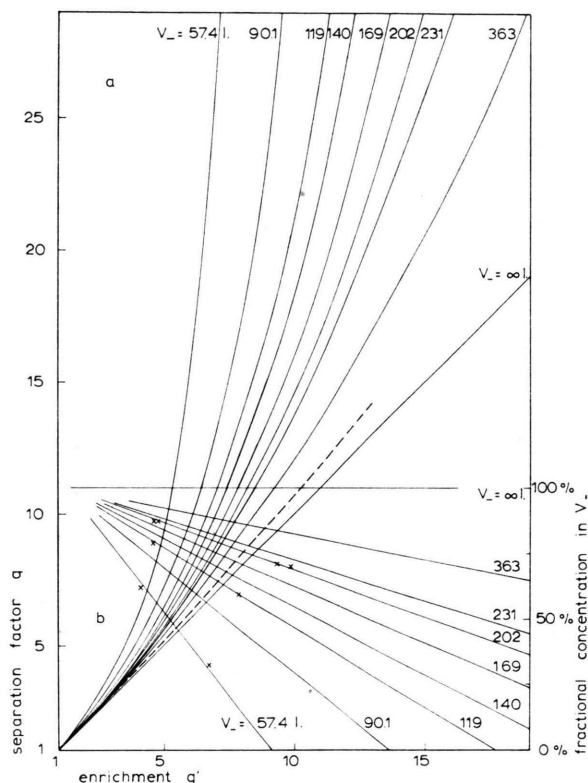


Fig. 8. a) Isotope separation factor q^{30} as a function of isotopic enrichment $q^{30'}$ for various storage volumes V_- . The conversion factor $q^{30'} \leftrightarrow q^{30}$ is determined by the depletion of the isotope considered in V_- (which is the same for all isotopic species having the same enrichment) as well as by the change in concentration of the common isotopic molecule $\langle 28 \rangle$ in V_+ (and V_-). — Effect of depletion in V_- . — — — Effect of decrease of $\langle 28 \rangle$ in V_+ for $V_- = \infty$. b) Depletion of heavy isotopes in storage volume V_- for various volumes and enrichments.

In Eq. (5) V_+ and V_c refer to the total volume of enriched gas and the total column volume, respectively. Since the average performance of the columns is nicely represented by column 1 (Fig. 6), q' for this column closely corresponds to the average enrichment. In Fig. 8 a the calculated graphs for volume correction are presented using the known volumes of the system. From Eq. (5) it can be seen, that the graphs for $\langle 29 \rangle$ when including the $\langle 28 \rangle$

concentration correction will be slightly different from those for $\langle 30 \rangle$, since for a certain value of q' the last factor in Eq. (5) is different.

The change of the separation factor as a function of time can be represented in good approximation by a simple exponential equation¹⁵.

$$(q - 1) = (q_e - 1)(1 - e^{-t/t_r}) \quad (6)$$

where q_e is the equilibrium isotope separation factor and t_r the relaxation time of the system. The exponential approach of q to an end value is due to the fact that an increasing isotopic concentration gradient has to be maintained over the column length. If $t \ll t_r$, Eq. (6) can be approximated by

$$(q - 1) = (q_e - 1)t/t_r. \quad (7)$$

Figure 7 shows that q' is proportional with time only for a rather short period. The relative difference between the enrichments slowly increases with time to about 16%.

The proportionality of q with time is somewhat better, indicating that the finite negative volume influences the enrichment obtained.

The discrepancies between the different enrichments (Fig. 7) are at least partially systematical and according to expectation. The thermal circulation was subsequently improved by installing a second heating element (250 W each) to circulate the gas through the top of the columns, since measurements showed that with only one element the gas in the circulation pipes close to the columns was $\cong 1.5$ times more depleted in the heavy isotopes than the reservoir gas in V_- . With the new circulation system the composition was equal within the measuring accuracy ($\cong 1\%$).

No further definite and quantitative conclusions can yet be drawn about the possible influence of wire temperature, sample extraction and extension of storage volume. The importance of a large reservoir V_- and a good circulation of the reservoir gas over the columns is obvious.

Calibration of the ^{14}C enrichment

After the thermal diffusion apparatus had been moved to Groningen a series of enrichments was performed in order to find a relation between the enrichment of ^{14}C and the stable isotopic molecules of mass $\langle 30 \rangle$ under the new conditions.

One difficulty in establishing a calibration relation is the fact that a proportional counter detects

a ^{14}C concentration (specific activity), while a mass-spectrometric measurement yields an isotope ratio. Thus in order to relate the experimentally determined changes in isotope ratio to the ^{14}C enrichment obtained, it is necessary to know the behaviour of the relevant isotopic molecules in the gas mixture and the influence of the system volumes on the enrichment [c. f. Equation (5)].

From Eq. (6) we find by elimination of t

$$\left(t = -t_r^{30} \ln \left\{ 1 - \frac{q^{30}-1}{q_e^{30}-1} \right\} \right) \\ 1 - \frac{q^{14}-1}{q_e^{14}-1} = \left\{ 1 - \frac{q^{30}-1}{q_e^{30}-1} \right\}^{t_r^{30}/t_r^{14}} \quad (8)$$

After rearrangement a series expansion gives

$$q^{14}-1 = a_1(q^{30}-1) + a_2(q^{30}-1)^2 + a_3(q^{30}-1)^3 + \dots \quad (9)$$

where

$$a_1 = \frac{(q_e^{14}-1)t_r^{30}}{(q_e^{30}-1)t_r^{14}}; \\ a_2 = \frac{(q_e^{14}-1)t_r^{30}(t_r^{14}-t_r^{30})}{(q_e^{30}-1)^2 2! (t_r^{14})^2}; \\ a_3 = \frac{(q_e^{14}-1)t_r^{30}(t_r^{14}-t_r^{30})(2t_r^{14}-t_r^{30})}{(q_e^{30}-1)^3 3! (t_r^{14})^3}.$$

The relation between the separation factors can thus be approximated by a polynome.

CO_2 gas prepared from shells by treatment with hydrochloric acid was used as a starting material for the calibration enrichments. The specific ^{14}C activity prior to enrichment was measured twice, giving a mean activity of $(77.88 \pm 0.24)\%$ of the standard activity. Four enrichments were carried out. The ^{14}C activity after the enrichment was determined, as well as the stable isotopic composition of the CO gas before and after enrichment. Due to the scatter in the mass spectrometric analysis on the CO samples the construction of a reliable calibration curve poses serious problems. This may be caused by impurities in the sample gas. The most serious is nitrogen, which is not easily removable and can not be detected, because it has the same mass as CO.

After oxidation of the enriched CO sample to CO_2 the isotopic composition was measured again. From this the isotopic composition of the enriched CO gas can be deduced. The mass (46) enrichment measured is about half that for mass (30) in the CO, because of dilution by oxygen with a natural

isotope ratio from the CuO furnace. The actual (46) enrichment factor of the CO_2 may be somewhat lower than expected from merely dilution in the CuO furnace, since during oxidation of CO exchange of oxygen between the CO– CO_2 and the CuO can also take place²³. The agreement between the results obtained from CO and CO_2 measurements is reasonable, although the results from the mass (46) measurements seem to be more consistent and agree better with Equation (9). Consequently, these will be used in the construction of the calibration curve.

First, δ^{45} and δ^{46} are calculated applying corrections for the presence of the tail from ion beam (44) under the mass (45) and (46) peaks and for the collection of ions of different masses by the B-collector (c. f. Reference 21). Secondly, the enrichments $q^{20'}$ and $q^{30'}$ are calculated assuming that the oxidation only involves the addition without fractionation of one oxygen atom per molecule CO from an oxygen reservoir of standard isotopic compo-

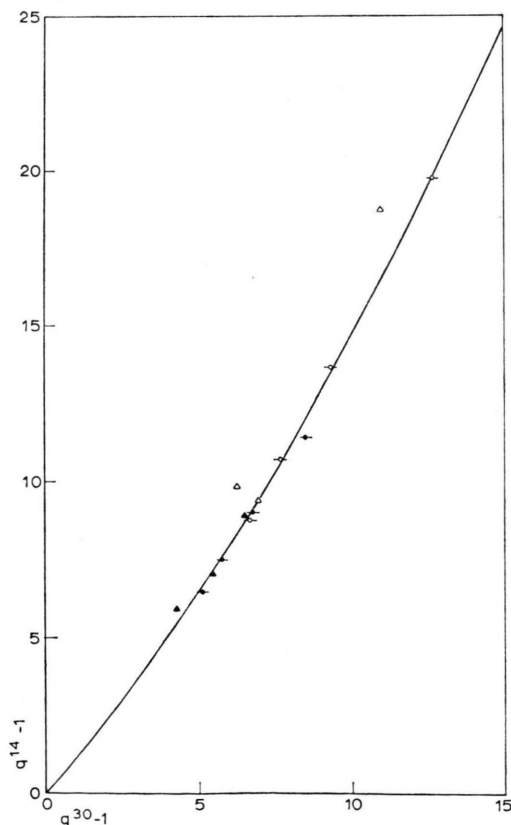


Fig. 9. Calibration curve $q^{14}-1 = (1.13 \pm 0.05)(q^{30}-1) + (0.035 \pm 0.005)(q^{30}-1)^2$. ● Enrichments and ○ separation factors Groningen. ▲ Enrichments and △ separation factors Amsterdam.

sition. As long as the isotopic exchange is small, these assumptions are acceptable. Using Eq. (5) the separation factors are obtained.

The ^{14}C enrichment $q^{14'}$ is found directly from the sample activities in the proportional counter before and after enrichment. Using Eq. (5) and the calculated $q^{20'}$ and $q^{30'}$ the separation factor q^{14} is obtained. In Fig. 9 $q^{14} - 1$ and $q^{14'} - 1$ are plotted versus $q^{30} - 1$ and $q^{30'} - 1$, respectively. Incorporating the point (0,0), a second order relation is needed in order to obtain a good fit:

$$q^{14} - 1 = (1.13 \pm 0.05) (q^{30} - 1) + (0.035 \pm 0.005) (q^{30} - 1)^2. \quad (10)$$

Apparently at least two terms of the series expansion are needed to give the calibration relation for the separation factors in the interval $1 < q^{14} < 20$. Since only 4 measurements are available, third and higher order terms cannot be determined with any accuracy.

The calibration relation obtained is independent of the storage volume V_- and can be used for all ^{14}C enrichment samples produced with the present columns.

At the time when the columns were still in operation in Amsterdam, 3 calibration measurements were made using as a starting material known mixtures of CO_2 from anthracite and recent wood and an oxalic acid-anthracite CO_2 mixture. The ^{14}C enrichment was then measured in Groningen and the mass (30) enrichment was determined in the Amsterdam laboratory from single collector mass spectrometer measurements on the CO gas before and after enrichment. The resulting separation factors are also given in Figure 9.

A comparison of the results is difficult, since in the course of the project several alterations have been made in the thermal diffusion apparatus. The equilibrium separation factor, for instance, depends on the length of the columns according to $q_e = e^{2AL}$, where L is the column length¹⁵.

Of the 3 earlier calibration points, one fits excellently and two give a somewhat lower q^{30} for a certain q^{14} . Although, as stated above, one should be careful in making comparisons, this gives support to the supposition that exchange of oxygen in the CuO furnace does not seriously influence the isotopic composition of the CO_2 . Otherwise larger q^{30} values would be obtained from the CO measurements in Amsterdam.

In earlier work with a small experimental thermal diffusion column, operated until equilibrium conditions had been reached, De Vries²² found:

$$\begin{aligned} \ln(q_e^{14})/\ln(q_e^{18}) \\ = \alpha(^{14}\text{C}^{16}\text{O}, ^{12}\text{C}^{16}\text{O})/\alpha(^{12}\text{C}^{18}\text{O}, ^{12}\text{C}^{16}\text{O}) \\ = 1.15 \pm 0.03. \end{aligned}$$

This relation only depends on the thermal diffusion factor α ; thus the same is true for the equilibrium separation factors q_e of the present apparatus.

Accuracy. If the relative accuracy in determining the isotopic composition of the enriched gas (either CO or CO_2) is 2%, a careful evaluation of the different factors influencing the final results shows this to be the main source of error. The standard deviation for $q^{30'}$ is then calculated as 1.9% which in combination with an uncertainty in the calibration relation of approximately 1% originating from the same source leads to a relative standard deviation for $q^{14'}$ of 2.1% for interpolation ($1 < q^{14} < 20$).

The range of the radiocarbon method

The residual radio-activity in samples of a radiocarbon age between 50,000 and 75,000 ranges from about $2 \cdot 10^{-3}$ to 10^{-4} times the original activity, which is already rather low. This means that the amount of recent contamination must be smaller than 50 ppm. We will distinguish between two groups of contamination: (i) sample contamination, which includes carbon containing materials having an age different from that of the sample, that are introduced into the sample in situ (humic acids, rootlets, carbonate) or during sample collection and transport; (ii) laboratory contamination, which comprises all foreign carbon introduced during sample handling in the laboratory.

Sample contamination

It is difficult to estimate the relative importance of this group of contaminants, since the amount of contamination can differ greatly from sample to sample. Therefore the possibilities of the occurrence of sample contamination should be investigated before the sample is taken and here the cooperation between the collectors of the sample and the dating laboratory is extremely important.

Although the chemical pretreatment that is routinely used in our laboratory²⁴⁻²⁶ (acid-alkali-

acid) removes most of the contaminations present, the reliability of a date for an event can only be established by measuring different samples from the same profile and corresponding samples from related profiles. A further indication about the trustworthiness of a high ^{14}C age is revealed by dating successive fractions of the alkali extract removed during the pretreatment. After the sample has been taken, it should obviously not be brought into contact with carbon containing materials such as cotton wool, paper, cloth, oil, varnishes, etc. In practice it turns out to be possible to keep the contamination of this type sufficiently low.

Laboratory contamination

This might originate from several sources, e.g. chemicals, demineralized water, combustion gases, contamination or memory effect in the combustion line, leakages in the vacuum systems, contamination in the reduction and oxidation system, etc. Since the laboratory treatment is essentially the same for every sample, the influence of any possible contamination can be detected by blank runs. Under routine conditions²⁰ a blank run of the combustion system yields between 0.1 and 0.3‰ of the normal amount of sample CO_2 .

This is well below the detection limit of normal radiocarbon dating, but becomes serious when thermal diffusion enrichment is to be used.

The first anthracite sample showed a measurable amount of radiocarbon after enrichment.

measured activity: $A_e = 0.082 \pm 0.039$ cpm,
 enrichment: $q^{14'} = 11.37 \pm 0.24$,
 apparent age: $t = 67,200 \pm \begin{smallmatrix} 5,000 \\ 3,100 \end{smallmatrix}$
 years (GrN 6533).

A blank run on the combustion line for one week gave 48.5 ml STP CO_2 gas.

This was added to a "dead" anthracite- CO_2 sample. The activity of this sample was 0.575 ± 0.044 cpm, resulting in an activity of the contamination of $190\% \pm 15\%$ (GrN 6594). A contamination of 0.2‰ of this carbon gives an age of 63,000 years to a sample of virtually infinite age. This might account for the finite dates obtained for anthracite in the period before 1967 and for the radiocarbon content of the anthracite mentioned above.

A thorough investigation (Table 2) showed that the gases of technical grade (N_2 and O_2) introduce

Table 2. Amount of CO_2 produced during a (blank) run in various parts of the combustion system.

Source	Fraction of total gas used in vpm			
	oxygen CO_2	CO_2 from hydro- carbon	nitrogen CO_2	CO_2 from hydro- carbon
Gas, technical quality	18	10 to 15	3	4
Gas, high purity, teflon membrane	—	≈ 15	—	—
The same with two cold traps -80°C	—	≈ 8	—	—
Rubber membrane	—	≈ 8	—	—
sodiumhydroxide solution	—	—	—	—
combustion tube		10–80		
potassium-permanganate		0–10		
vacuum section		0		

foreign carbon into the sample, that cannot be simply removed with an alkali wash bottle, since part of it is present as hydrocarbons. Therefore high purity gases should be used and, in addition, passed through -80°C traps.

The main source of contamination, however, appeared to be in the combustion tube. The condensation of hydrocarbons in "cold" parts of the system during the degassing procedure causes a memory effect. If the combustion tube is cleaned thoroughly before every combustion and only "old" samples are admitted to the system, the amount of radiocarbon introduced is negligible (blank run: $\text{CO}_2 < 50$ vpm based on the total volume of O_2 passed through the system). In the sample CO_2 the resulting carbon contamination is higher because of the excess of oxygen introduced for combustion, but if the foreign carbon comes from previously combusted old samples this introduces no measurable error.

After the necessary precautions mentioned above had been taken two more anthracite samples were made. The results are given in Figure 10.

The average results obtained are as follows:

enriched anthracite II: $A_e = 0.023 \pm 0.030$ cpm,
 enrichment: $q^{14'} = 10.38 \pm 0.22$,
 according to 2σ convention: $t > 66,300$ years
 (GrN 6680),

apparent age: $t \approx 76,600 \pm \begin{smallmatrix} \infty \\ 6,800 \end{smallmatrix}$ years,

enriched anthracite III: $A_e = 0.0245 \pm 0.0139$ cpm,
 enrichment: $q^{14'} = 12.81 \pm 0.27$,

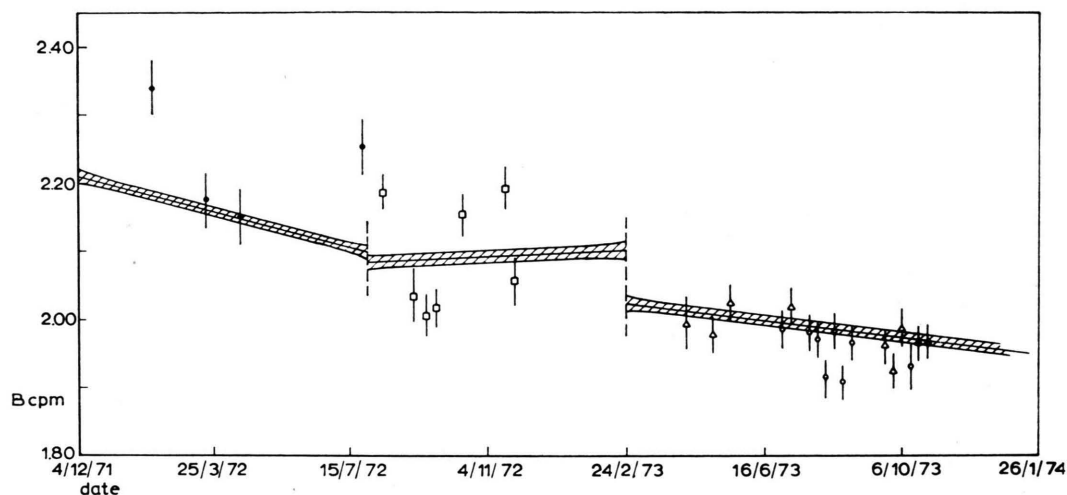


Fig. 10. Background 1.71 proportional counter with results anthracite enrichments. ● Enriched anthracite I, GrN 6533; □ enriched anthracite II, GrN 6680; ○ anthracite III, GrN 6851; △ enriched anthracite III, GrN 6808.

according to 2σ convention: $t > 71,700$ years (GrN 6808),
 apparent age: $t \cong 77,800 \pm \begin{matrix} 6,600 \\ 3,800 \end{matrix}$ years.

These results indicate that as far as laboratory contaminations are concerned radiocarbon dates up to about 75,000 years can be obtained. Normally the contamination in the combustion system must have been the main source of error. However, some erroneous results obtained earlier²⁷ cannot be explained by this and therefore must be ascribed to other causes (e.g. the filling of the zinc furnace which is renewed for every sample).

The comparison of the results of GrN 6851 and GrN 6808 proves that CO_2 prepared from anthracite contains no measurable amount of radiocarbon and can therefore be used for background measurements.

In the interpretation of the results of enrichment datings it should be born in mind, that the contamination activity found in anthracite- CO_2 is possibly not zero. For old samples with a measured activity just above 2σ this may lead to discrepancies between the date obtained and the true age of the sample of a few thousand years. Since laboratory contamination is approximately the same for all samples this is hard to detect. The consistency of the results, however, is not affected.

Summary

Due to differences in performance found between the individual "identical" columns an experimental

determination of the enrichment factor is necessary. The increase of the separation factor with time is found to be linear during the first three weeks and almost so during four. Depending on the storage volume V_- used, the obtained enrichment lags behind. From a series of four enrichments a calibration relation for the separation factors has been obtained,

$$q^{14} - 1 = (1.13 \pm 0.05) ((q^{30} - 1) + (0.035 \pm 0.005) (q^{30} - 1)^2).$$

Once the isotopic enrichments $q^{29'}$ and $q^{30'}$ of a sample have been measured mass-spectrometrically the ^{14}C enrichment factor can be calculated with a relative accuracy of about 2% by using the equation

$$q^{14'} = q^{29'} \frac{C_{V-}^{29*}}{C_0^{29}} \cdot \frac{C_{V-}^{28*}}{C_{V-}^{28}}.$$

twice and the relation $q^{14} - q^{30}$ given above.

With the present apparatus samples containing a minimum amount of 43 g of carbon can be enriched. From a normal sample containing 130 g of carbon a gas sample of 6.3 l NTP (one proportional counter filling) is obtained, which is enriched in ^{14}C by a factor of 7 in three and a factor of 9 in four weeks.

During a routine procedure for ^{14}C samples a detectable amount of contamination would be introduced in the sample. A special treatment reduces this laboratory contamination to below the detection limit and makes dates up to 75,000 years attainable.