Enrichment of $^{14}CH_4$ by Thermal Diffusion for Use in Radiocarbon Dating *

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By means of a thermal diffusion column the range of the radiocarbon dating method can be extended by about 20 000 years. In order to calculate suitable dimensions and operation conditions, a theory of nonlinear enrichment is derived. On the basis of a formula which describes the dependence of the enrichment factor on time and the characteristic values of the column, a concentric column of 11 m length was constructed. The enrichment factors obtained for $^{13}CH_4$ as a function of time (up to 400 h) and pressure (150—1500 Torr) and for $^{14}CH_4$ at 740 Torr and up to 1000 h are presented and discussed. A method is described to indirectly determine the enrichment factor in the stationary state and the characteristic time.

1. Introduction

Due to the low specific activity of recent carbon of about 14 cpm/g and the half life of carbon-14 of 5730 years[1] the application of the radiocarbon dating technique is limited to about 60 000 years[2]. In order to extend the radiocarbon dating limit we took up anew the problem of enrichment of carbon-14 by employing a Clusius-Dickel thermal diffusion column. The essential problem lies in the determination of the enrichment factor with sufficient accuracy.

The theory of thermal diffusion of Jones and Furry[3] yields the separation factor in the stationary state as a function of the characteristic features of a diffusion column. However, this theory cannot be applied for this purpose because of the deviations of the experimental values from theory and the difficulty in reproducing[4–6].

Therefore methods have been worked out to determine the enrichment indirectly. Haring et al.[7] in 1958 used the easily measureable enrichment of the isotopic molecule $^{12}C^{18}O$ to determine the enrichment of $^{14}C^{16}O$. Using five columns of 4,3 m length, connected in parallel, and a total amount of 350 l carbonmonoxide, they receive 8 l of CO enriched by a factor of 16 within two months.

Another effort to improve the reproducibility is based on the experience that the initial transport is in good agreement with the theory[4, 5]. Confining himself to the range where the concentration increases linearly with time, Dickel[8] was able to predict the enrichment factors that he actually obtained with the "transport method". Using a concentric column of 11 m length he obtained for $^{14}CH_4$ an enrichment factor of 2,2 within 8 days.

As this technique suffers from rather modest enrichments we extended the enrichment into the nonlinear range, being careful to ensure that the stationary state is not approached too closely.

For this purpose it was necessary to derive a formula which describes the enrichment factor as a function of time and characteristic features of an enrichment apparatus such as initial transport, separation factor, total amount of methane and enriched amount of methane. The dimensions of the enrichment apparatus and the operation conditions should be chosen in such a way that an enrichment factor of 8 can be reached in the quasilinear range within a few days. An enrichment factor of $8 = 2^3$ corresponds to three half lives, equivalent to an extension in age of 17 200 years. First results have been published in[9–11]. An enrichment apparatus for methane was also constructed by Erlenkeuser[12] in Kiel and Felber and Pak[13] in Vienna.

2. Theory of Nonlinear Enrichment

2 a) *The Enrichment Factor*

The theory of the Clusius-Dickel thermal diffusion column has been treated by many authors[3, 14–16]. In this paper we use the notation of Dickel[16].

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Using a collecting container V_b, the enrichment factor A of $^{14}CH_4$ in V_b is given as

$$A(t) \equiv c_b(t)/c_0 = \int_0^1 \frac{\int_t^0 \tau(t)\,\mathrm{d}t}{c_0\,\varrho_b\,V_b} + 1 \qquad (1)$$

[$\tau(t)$ transport in g/sec, $c_b(t)$, c_0 mole fraction of $^{14}CH_4$ in V_b at time t and $t=0$, respectively, $c_0\,\varrho_b\,V_b$ total amount of $^{14}CH_4$ in V_b in grams at time $t=0$ and ϱ_b density in V_b]. To evaluate (1), we make use of the transport equation[16] under the assumption $c(z,t) \ll 1$

$$\tau(z,t) = \tau_a^*\,c(z,t) - K\,\mathrm{d}c(z,t)/\mathrm{d}z \qquad (2)$$

(K remixing coefficient, z coordinate along the axis of the column).

Setting $\mathrm{d}c(z,t)/\mathrm{d}z = 0$ and $c(z,t) = c_0 = \text{constant}$, we get a simple special case where $A(t)$ increases linearly with time as described formerly[8].

In order to obtain a general formula for the enrichment factor $A(t)$, we begin with the integration of the transport equation (2), assuming the transport τ to be independent of the coordinate z. Thus (2) becomes a linear differential equation and yields after integration:

$$c(z,t) = \frac{\tau(t)}{\tau_a^*}\left(1 - \exp\left(\frac{\tau_a^*}{K}\,z\right)\right) + c_t \exp\left(\frac{\tau_a^*}{K}\,z\right) \qquad (3)$$

(c_t mole fraction of $^{14}CH_4$ at the top end of the column). At $z=L$ we obtain:

$$c_b(t) = [\tau(t)/\tau_a^*]\,(1-q_e) + c_t(t)\,q_e \qquad (3\,a)$$

($q_e = \exp\{\tau_a^*\,L/K\}$ separation factor in the stationary state, L column length).

This assumption means that no molecules are accumulated in the column, i. e. that the transport from the storage container into the column is equal to the transport from the column into the collecting container. This leads to:

$$\tau(t) = -\varrho_t\,V_t\,\mathrm{d}c_t(t)/\mathrm{d}t = +\varrho_b\,V_b\,\mathrm{d}c_b(t)/\mathrm{d}t \qquad (4)$$

[V_t(t = top), V_b(b = bottom) volume of the storage and collecting container, ϱ_t, ϱ_b densities]. In practice this condition is fulfilled if the amount of gas in the column is considerably smaller than the amount of gas in the storage and collecting container, $\varrho\,V_{Tr} \ll \varrho_b\,V_b, \varrho_t\,V_t$. Differentiating (3 a) with respect to t and replacing the resulting values of $\mathrm{d}c_t(t)/\mathrm{d}t$ and $\mathrm{d}c_b(t)/\mathrm{d}t$ by means of (4), we get a separable differential equation of the transport τ. Integration yields

$$\tau(t) = \tau_a^*\,c_0\,e^{-t/T}, \qquad (5)$$

where

$$T = \frac{\varrho_b\,V_b}{\tau_a^*}\,\frac{n(q_e-1)}{n+q_e} \quad \text{and} \quad n = \frac{\varrho_t\,V_t}{\varrho_b\,V_b} = \frac{m_t}{m_b}\,. \qquad (6, 7)$$

If (5) is substituted into (1), we obtain the enrichment factor $A(t)$:

$$A(t) = [n(q_e-1)/(n+q_e)]\,(1-e^{-t/T}) + 1\,. \qquad (8)$$

2 b) *Taking the Volume of the Column into Account*

In reality there is always an enrichment in the column itself, a fact which can be taken into account by a fictitious increase of the volume of the collecting container by a reduced volume of the column $V_{Tr}^* = k\,V_{Tr}$. Because of this increase of the collecting container, the volume of the column can be neglected and $\tau(t,z)$ can be considered as independent on the coordinate z. Furthermore, if we take into account that the densities in the column and the collecting container are different, we must replace $\varrho_b\,V_b$ by $\varrho_b\,V_b + k\,\varrho\,V_{Tr}$ in (1) and (4) and obtain instead of (6) and (7):

$$T = \frac{\varrho_b\,V_b + k\,\varrho\,V_{Tr}}{\tau_a^*}\,\frac{n(q_e-1)}{n+q_e}, \quad n = \frac{\varrho_t\,V_t}{\varrho_b\,V_b + k\,\varrho\,V_{Tr}} \qquad (6\,a,\ 7\,a)$$

where $$k = (\bar{A}_{Tr} - 1)/(A-1) \leqq \tfrac{1}{2} \qquad (9)$$

($\bar{A}_{Tr}$ mean value of the enrichment factor in the column).

The upper limit $k = 1/2$ is valid for a linear concentration gradient which exists in good approximation at the beginning of the enrichment. This approximation can be controlled by means of the time dependence of the enrichment in the linear range (see part 6 b).

2 c) *Special Cases of A(t)*

We now consider some special cases of (8). Taking into account (6 a), the expansion of (8) into a power series yields in the case $t \ll T$:

$$\mathrm{d}A/\mathrm{d}t = m = \tau_a^*/(\varrho_b\,V_b + k\,\varrho\,V_{Tr})\,. \qquad (11)$$

This equation describes the slope of the enrichment in the linear range. If $t \to \infty$, we obtain from (8) the enrichment factor in the stationary state A_e which can be derived also from the law of conservation of mass[11]:

$$A_e = \frac{q_e(n+1)}{q_e+n} \,. \qquad (12)$$

The fundamental limits of the enrichment are given by two special cases of (12):

If $q_e \to \infty$, we obtain $A_e = n+1$, (12 a)

if $n \to \infty$, we obtain $A_e = q_e$. (12 b)

Together with (12) Eq. (8) can be written as

$$(A-1) = (A_e-1)\,(1-e^{-t/T}) \,. \qquad (13)$$

From (11), (12) and (6 a) follows:

$$T = \frac{A_e-1}{m} \,. \qquad (14)$$

2 d) The Overall Enrichment Factor

Considering the overall enrichment factor $\bar{A}$ in the collecting container and the separation column, we do not find such a simple relation between the enrichment factor and the separation factor as predicted by (8) and (12). From the law of conservation of mass a simple relation is derived between the enrichment in the storage container $A_t(t) \equiv c_t(t)/c_0$ and the overall enrichment $\bar{A}(t) \equiv \bar{c}(t)/c_0$,

$$\bar{A}(t) = \bar{n}+1-\bar{n}\,A_t(t) \,, \qquad (15)$$

where $\bar{n} = \varrho_t V_t / (\varrho_b V_b + \varrho V_{Tr})$. (7 b)

As $A_t(t)$ can be measured directly, $\bar{A}(t)$ can be determined experimentally by means of (15).

In order to calculate $\bar{A}(t)$ we use a relation analogous to (15) between the enrichment in the storage container $A_t(t)$ and the enrichment in the collecting container $A(t)$:

$$A(t) = n+1-n\,A_t(t) \,, \qquad (15\,a)$$

where n is given by (7 a). Eliminating $A_t(t)$ in (15) and (15 a) we obtain:

$$\bar{A}(t) = 1-\frac{\bar{n}}{n}+\frac{\bar{n}}{n}\,A(t) \qquad (16)$$

where $A(t)$ is given by (8).

3. Dimensions of the Enrichment Apparatus

Suitable dimensions of the enrichment apparatus, column length L, distance between the hot and the cold wall d, cross section Q, volume of storage and collecting container, result from (11) and (12). The increase of the enrichment in the linear range is proportional to the initial transport τ_a^* which is given by (17) and (18)[16]:

$$\tau_a^* = \frac{4}{15}\,\alpha \ln \frac{T_i}{T_a}\,\varrho\, D\, \frac{d}{u}\, P_\tau\, \varphi\, Q \qquad (17)$$

$$u = \frac{\bar{w}\,d}{D} = \frac{g}{192\,\eta\, D}\,\varrho\, d^3 \ln \frac{T_i}{T_a} \qquad (18)$$

(α thermal diffusion factor, T_i, T_a temperature of the inner and outer wall, D diffusion coefficient, P_τ, P_K correction terms of parasitic remixture[4], φ, ψ, χ conversion factors from the planar to the radial separation problem[16], $\bar{w}$ mean circulation velocity, g acceleration due to gravity, η viscosity, Q cross section of the column).

According to (12), the enrichment factor in the stationary state A_e depends on q_e and n. If the optimum density is chosen with regard to q_e, the latter value depends exponentially on the relation between the column length and the distance between the hot and the cold wall d as shown in (19)[16]:

$$q_e = \exp\left(\frac{\tau_a^*}{K}\,L\right) = \exp\left(\frac{4}{15}\,\alpha \ln \frac{T_i}{T_a}\,\frac{u}{0{,}1\,u^2\,\psi\, P_K+\chi}\,\varphi\, P_\tau\, \frac{L}{d}\right) . \qquad (19)$$

The other parameters are determined by the nature of the gas, the geometry of the column and the maximal possible temperature.

Keeping $k\,V_{Tr} = k\,Q\,L$ constant, the mass ratio n is determined due to (7 a) by V_b which is determined by the volume of the ^{14}C-counter, and by V_t which is essentially determined by the total amount of the methane sample.

The dimensions of our enrichment apparatus were chosen in such a way that, on the one hand, an enrichment factor A in the collecting container is established in the quasilinear range within about 10 days and that, on the other hand, the total amount of methane required is not too high.

The distance between the hot and the cold wall was chosen not to exceed a minimum of $d = 5$ mm, since otherwise the relative deviations $\Delta d/d$ would be too high. Therefore, the column length was chosen to be 10.9 m, taking into account the deviations of the experimental and theoretical values of q_e[5, 6].

4. The Enrichment Apparatus

To obtain a great initial transport, we used a concentric column made of brass with a diameter of the hot tube of $d_i = 45 \pm 0.15$ mm, wall thickness 3 mm and a diameter of the cold tube $d_a = 55 \pm 0.15$ mm, wall thickness 1.5 mm. Because of the thermal expansion, the hot tube is soldered to the cold tube at the top end and is suspended fully floating in the cold tube. The distance between both tubes is maintained by radial spacing cones, three at every 1.2 m, with a length of 4.8 ± 0.1 mm. Therefore, the deviations from the theoretical value of the distance are -6% and $+12\%$ in the most unfavorable case. The column is connected with the storage and the collecting container by means of thermal convection loops and is heated by heating wires ($\phi = 1.2$ mm, length 11 m). In order to achieve a homogenous temperature distribution the heating wires are arranged coaxially to the hot tube by ceramic multiple hole tubes. Thermal expansion of the wires is compensated by means of a suitable suspension. The power consumption of 6 kW yields a temperature of the hot wall $T_i = 582$ °K.

Methane was chosen for the enrichment of ^{14}C because it can reliably be prepared, has a fairly high thermal diffusion coefficient and very good proportional counter gas qualities. Up to now we used tank methane of high purity (99.95%). The ratio of $^{13}C/^{14}C$ was analysed by means of a mass spectrometer (GD 150 MAT Bremen). The content of ^{14}C in the samples was counted in a low level counting device (Beckmann Instruments, Sharp Laboratories Division). A more detailed description of the enrichment apparatus can be found in [11].

5. Experimental Results

The apparatus was first tested by measuring the enrichment factor of $^{13}CH_4$ as a function of time (up to 400 h) at 16 different values of the pressure (150 – 1500 Torr). The maximum enrichment factor obtained was 5.77 after 16 days at a pressure of 1000 Torr (Fig. 2, Nr. 11). In the linear range the experimental values are situated on a straight line within the experimental error of 2 – 4% (Figure 1). Reproducibility was found within the same limits. These results already confirm qualitatively the time dependence of A according to (8, 11, 12). The initial slope increases with increasing pressure, but at the optimum pressure (740 Torr) with respect to q_e, we obtain the maximum length of the linear range (Figures 1, 2).

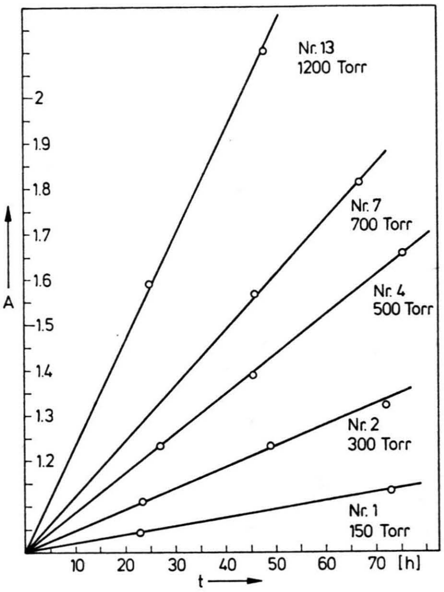

Fig. 1. $^{13}CH_4$, Enrichment factor A as a function of the time t.

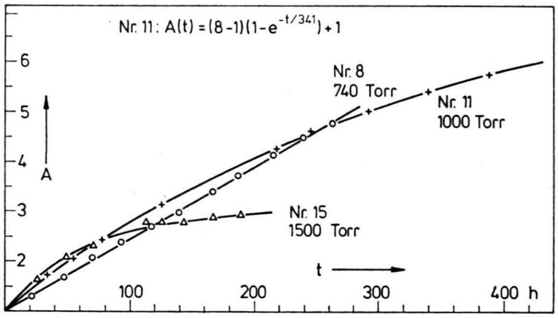

Fig. 2. $^{13}CH_4$, Enrichment factor A as a function of the time t.

For the enrichment of $^{14}CH_4$ we used artificially-^{14}C-enriched methane ($10^{-7}\%$ $^{14}CH_4$). In this way we were able to count small samples (20 cm^3) taken during the enrichment. Using a total amount of 169 g of methane (740 Torr), we received in the collecting container 1.27 g of methane which was enriched by a factor of 8 within 10 days and a factor of 20.6 within 45 days. Even then the stationary state had not yet been established (Fig. 3, curve 1).

The overall enrichment factor of 5 g methane in the collecting container and the column, calculated according to (15, 16) was 8 after 24 days and 11.4 after 45 days (Fig. 3, curve 2).

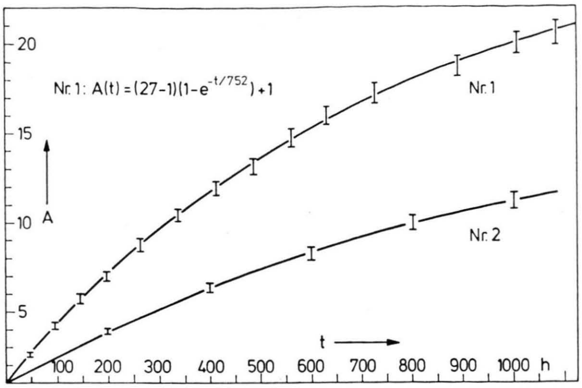

Fig. 3. $^{14}CH_4$, Enrichment factor A as a function of the time t. Nr. 1: Collecting container; Nr. 2: Collecting container and separation column.

6. Comparison with the Theory

6 a) Calculated Values

To calculate the values of the initial transport according to (17) and the separation factor according to (19), we used the following data:

$V_t = 250$ l, $V_b = 2$ l, $Q = 7.85$ cm², $L = 10.9$ m, effective column length 10.6 m, mean temperature in the column $\overline{T} = 437 \pm 5$ °K, $\ln(T_i/T_a) = 0.689 \pm 0.017$, $\varrho = (4.47 \pm 0.05)\,10^{-4}$ g/cm³ at 760 Torr and 437 °K, $\varrho_t = \varrho_b = 1.46\,\varrho$, $\eta = (1.51 \pm 0.02)\,10^{-4}$ poise, $D = 1.406\ \eta/\varrho = 0.474$ cm²/sec, $\alpha\,(^{12}CH_4 - {}^{13}CH_4) = (7.7 \pm 0.1)\,10^{-3}$ from [12], $\alpha\,(^{12}CH_4 - {}^{14}CH_4) = (15 \pm 0.2)\,10^{-3}$, $\varphi = 1.086$, $\psi = 1.126$, $\chi = 1.013$ calculated according to [16].

Using a value of $k = 1/2$ we get according to (7 a) a value of $n = 50$.

The above standard deviations are due to the inaccuracy of the data and, additionally, to the inaccuracy of the mean temperature if the data are temperature dependent. The critical value is the thermal diffusion coefficient α, of which different values are to be found in literature [17]. The most exact seems to be the value of Erlenkeuser [12] which has, however, still an error of 3 – 5%.

Therefore, we obtain as standard deviation of the initial transport ±5% and of the slope m according to (11) ±4.5%. The error of the separation factor q_e (19) is considerably higher, because it depends exponentially on the above values. In addition parasitic remixing effects have a high influence [4], and the effective length of the column cannot be determined exactly. Therefore the calculated values of q_e are only recommendations and much higher than the experimental ones.

6 b) The Initial Transport

From (17) and (18), the initial transport is proportional to the square of the density. Therefore, according to (11), the slope of the enrichment in the linear range m is proportional to the density and to the pressure.

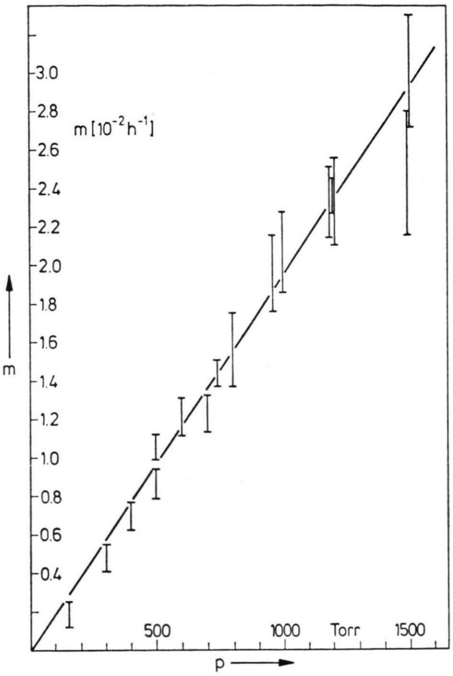

Fig. 4. $^{13}CH_4$, Slope of the enrichment in the linear range m as a function of the pressure p.

In Fig. 4 the experimental values of m are plotted versus the pressure. The standard deviations of m of 4 – 10% are calculated from the standard deviations of the enrichment factors and the different length of the linear range. As required by the theory, the points are situated on a straight line. Its slope is 5% lower than its theoretical value (Tab. 1) which has been calculated according to (11), using a value of $k = 1/2$.

Tab. 1. Experimental (I) and theoretical (II) values of m/ϱ [cm³/gh].

	I	II
$^{13}CH_4$	33.1 ± 1.7 [1]	35.3 ± 1.6 [7]
$^{14}CH_4$	74.0 ± 3.5 [3]	68.5 ± 3.1 [2]

[1] value from Fig. 4, [2] standard deviation due to 6 a, [3] mean value of three enrichments at 740 Torr.

6 c) The Enrichment Factor in the Stationary State

Because the stationary state is attained only asymptotically the corresponding value of the enrichment factor could not be measured directly. An indirect determination is possible in the following way:

Equation (13) can be transformed to:

$$\ln\left[(A_e-1)/(A_e-A(t))\right]=t/T\,. \qquad (20)$$

From the experimentally determined time dependence of A, the value of A_e can be predicted within narrow limits in two cases (Fig. 2, Nr. 11, Fig. 3, Nr. 1). One arbitrary value of A_e within these limits is substituted in (20) and $\ln(A_e-1)/[A_e-A(t)]$ is plotted versus the time t, making use of the measured values of $A(t)$. This procedure is repeated with different values of A_e (Figure 5). The correct value of A_e is characterized by the fact that the result is a straight line, having the slope $1/T$. As shown in Fig. 5, the value of A_e can be determined unambiguously since the curvature changes from concave to convex at the correct value of A_e. As expected, the value of A_e and, therefore, due to (14), the value of T are essentially lower than the theoretical ones (Table 2). This is caused by the fact that the separation factor in the stationary state q_e, which can be established experimentally, is in general much lower than its theoretical value $^{4-6}$ and A_e depends on q_e according to (12).

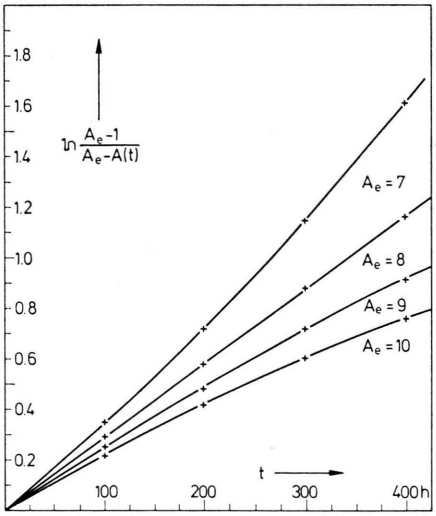

Fig. 5. $^{13}CH_4$, Nr. 11, Determination of the enrichment factor A_e in the stationary state (s. part 6 c).

Tab. 2. Experimental (I) and theoretical (II) values of A_e and T.

	$^{13}CH_4$, 1000 Torr I	$^{13}CH_4$, 1000 Torr II	$^{14}CH_4$, 740 Torr I	$^{14}CH_4$, 740 Torr II
A_e	8 ± 0.5	18.3	27 ± 1	89
$T[h]$	341	749	752	1162

Using the experimental values of A_e and T, the calculated time dependence of A according to (13) corresponds well with the measured points, as shown in Fig. 2, Nr. 11 and Fig. 3, Nr. 1.

$$^{13}CH_4,\ 1000\ \text{Torr:}\ A(t)=(8-1)(1-e^{-t/341})+1$$
$$^{14}CH_4,\ \ 740\ \text{Torr:}\ A(t)=(27-1)(1-e^{-t/752})+1$$
where $t[h]$

7. Discussion

In the range where the enrichment increases linearly with the time, accordance with the theory was observed. This can be considered as a verification of the assumption we made concerning the reduction factor k. The enrichment factor in the stationary state was, as expected, considerably lower than its theoretical value. Using the indirectly determined values of the enrichment factor in the stationary state and the characteristic time, the calculated and measured time dependence of A coincide over the whole range. Thus, the wole range can be used for the ^{14}C enrichment. This is of special importance with regard to a high exploitation of the ^{14}C sample (Table 3).

Tab. 3. Values of the enrichment factor A and the sample exploitation R for the gas in the collecting container (1—3) and in the collecting container and the column together (4—5).

Nr.	total amount of carbon [g]	Enriched amount of carbon [g]	t [d]	A	R [%]
1	127	0.95	10	8	6
2	127	0.95	45	20.6	16
3	127	0.95	$t\gg T$ [1]	27	21 [2]
4	127	3.76	23	8	25
5	127	3.76	45	11.4	35
6	127	3.76	$t\gg T$ [1]	15	46 [2]

[1] $T=31.33\ d$, [2] stationary state.

An essential problem concerning the practical application of the enrichment lies in the high amount of ^{14}C which is necessary to enrich one proportional counter filling by a factor A. We define the sample exploitation R as the percentage of the total amount of $^{14}CH_4$ molecules which can actually be counted in the proportional counter. If m_0 is the total amount of gas, m_e the enriched amount of gas and A the enrichment factor, the sample exploitation is given by:

$$R[\%] \equiv A\, m_e/m_0 \,. \tag{21}$$

In the case of an infinite separation factor the value of A has a maximum of $A_{\max} = m_0/m_e$, equivalent to $R = 100\%$. In practice, R is essentially lower and attains its maximum value in the stationary state (Table 3).

In the cases Nr. 1 – 3 the values of the enrichment factor A are higher than in the cases Nr. 4 – 6 and those of the sample exploitation are lower, because the enriched gas in the column is not used. If we keep the values of A and m_e constant, an increase of R corresponding to a decrease of m_0 will only be possible if the separation factor of the column is increased.

This would be feasible by an increase of the column length or, if we keep the column length constant, by a more precise construction of the column.

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