

# Radiocarbon

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## OPTIMUM OPERATING CONDITIONS OF $^{14}\text{C}$ -METHANE ISOTOPE ENRICHMENT BY CONCENTRIC TYPE THERMAL DIFFUSION COLUMNS FOR USE IN RADIOCARBON DATING

HELMUT ERLLENKEUSER

Institut für Reine und Angewandte Kernphysik,  
 $^{14}\text{C}$  Laboratory, University of Kiel  
Olshausenstrasse 40-60, 2300 Kiel, Germany

**ABSTRACT.** The optimum operating conditions providing minimum run-time and running costs have been studied theoretically for a thermal diffusion plant to be used for the enrichment of the radiocarbon isotope from finite sample size.

The calculations are based on a simple approximate model of the enrichment process, regarding the isotope separation column as operating under quasi-stationary state conditions. The temporal variation of the isotope accumulation is given by a single exponential term. From comparison with the numerical solution of the separation tube equation, approximate models of this simple type appear hardly sufficient for analytical work but seem well suited for optimization calculations. For column operation not too close to the equilibrium state, the approximate run-times were found accurate within 0.2 d.

The approximate model has been applied to a column of the concentric type, operated on gaseous methane. Cross-section configuration and temperatures were not varied (hot and cold wall radii: 2.0 and 2.6cm, respectively; hot and cold wall temperatures: 400°C and 14°C, respectively). The column transport coefficients used were derived from measurements. Run-time was minimized by optimizing both the operating pressure and the sample collection mode for different total sample size (range studied: 24 to 100 g), mass of enriched sample (1.8, 2.4, and 3.0 g), enrichment factor (12, 15, and 20) and column length (8 to 18 m). Optimum working pressures are between 1 and 2 atm. Usually, about 90 percent of the enriched sample mass is extracted favorably from the column itself, the length of the sampling section being about 2.5 to 5 m. Typical runtimes are between 3 days and 2 weeks, and isotope yield may reach 90 percent.

Optimum operating conditions have also been calculated for other column configurations reported in literature and are compared with the experimental results.

### INTRODUCTION

The extension of the radiocarbon dating method beyond 50,000 yrs B.P. and the improvement of the statistical accuracy of the  $^{14}\text{C}$  measurements for samples older than, say 20,000 yrs is of particular interest with regard to the history of the Earth's climate during the past 100,000 yrs. This period of time particularly, because of its proximity to the present and the availability of the  $^{14}\text{C}$  isotope for age determination, might provide sufficient data to elucidate the interrelationship of the natural systems controlling the climate and might further allow us to elaborate a model of the climate dynamics, provided reliable and detailed time scales of the climatic variations are available.

From the present state of the measuring technique, the extension of the radiocarbon method seems best achieved by making use of both iso-

tope enrichment and high sensitive  $^{14}\text{C}$  counting. Accordingly, several authors have been engaged in carbon-14 enrichment by thermal diffusion (deVries, Haring, and Slots, 1956; Haring, deVries, and deVries, 1958; Dickel, 1958, 1962; Pak, ms; Erlenkeuser, 1971a and ms; Felber and Pak 1973; Dickel and Kretner, 1973; Kretner, ms; Grootes and others, 1975). Successful application of this method has been reported recently by Grootes (ms) and Stuiver, Heusser, and Yang (1978).

Most of the previous attempts suffer greatly because of the large amount of radiocarbon sample required and the rather long run-times, which make isotope enrichment by thermal diffusion appear to be a method not particularly suitable for routine dating. However, as pointed out earlier (Erlenkeuser, 1971a and ms, 1976) the expenditure of sample size, run-time, and energy consumption may be reduced greatly by appropriate selection of the working conditions. We have taken up the problem of optimization anew and have studied it theoretically in greater detail than before on the basis of an approximate model of the isotope enrichment process in a thermal diffusion column.

The results show that samples up to a few g of mass may become enriched by a factor of 12 or so within a short period of time, roughly about a week, providing an isotope yield up to 90 percent. Still, it is obvious, that in spite of this high efficiency the total amount of the radiocarbon sample required appears very large and can hardly be met for many problems to be studied, such as the dating of selected foraminifera tests from deep sea cores. A solution of these problems, in a way quite different from conventional radiocarbon techniques, might be provided by the particle accelerators as used in high energy physics. This method, recently suggested by Muller (1977) and Bennett and others (1977), utilizes the large fraction of  $^{13}\text{C}$  atoms not yet decayed and hence will require a much lower amount of sample, on the order of 1 to 100 mg.

#### APPROXIMATE MODEL OF THE ENRICHMENT PROCESS

The thermal diffusion plant for the enrichment of radiocarbon from samples of finite size consists of the separation column, a reservoir for storing the bulk of the sample at the negative end of the column, and, possibly, a smaller sampling volume at the opposite end, where the isotope will become concentrated (positive column end). Details have been given elsewhere (Henseler, ms, 1973; Erlenkeuser, 1976; Grootes, ms). The enrichment plant is operated on a suitable gas, such as methane or carbon monoxide prepared from the radiocarbon sample. For these gases, the heavier isotopic molecule will be transported downward and will be found enriched in the lower part of the column.

The theory of the thermal diffusion column has been worked out by Jones and Furry (1946). In a binary mixture of isotopic molecules, the transport  $\tau$  of the species of interest along the column at height  $z$  is given by the transport equation

$$\tau = H c (1 - c) - K c_z \quad (2.1)$$

where

- $c$ : concentration (molar fraction) of the isotope considered
- $c_z$ : partial derivative with respect to  $z$
- $z$ : longitudinal coordinate of the column, counted in the direction of increasing concentration.

The transport coefficients  $H$ ,  $K$  depend on the characteristics of the column cross section, that is the radii of the hot and cold walls, the temperatures, and the transport properties of the gas at the height  $z$  considered, and are commonly independent on  $z$ .

Introducing the equation of continuity

$$-\mu c_t = \tau_z \quad (2.2)$$

where

- $\mu$ : mass of gas per unit length of column
- $c_t, \tau_z$ : partial derivatives with respect to time  $t$  and  $z$ , respectively

we obtain the separation tube equation:

$$-\mu c_t = H c_z (1 - 2c) - K c_{zz} \quad (2.3)$$

where

- $c_{zz}$ : 2d partial derivative with respect to  $z$

The initial concentration is

$$c(t = 0, z) = c_0 \quad (2.4)$$

and the boundary conditions are

$$\begin{aligned} \text{for } z = 0: \tau(t, z = 0) &= -M_- \frac{dc_-}{dt} \\ \text{for } z = L: \tau(t, z = L) &= M_+ \frac{dc_+}{dt} \end{aligned} \quad (2.5)$$

- $c_-, c_+$ : concentrations at the negative and positive column end, respectively
- $M_-, M_+$ : mass of gas in the negative and positive reservoir, respectively
- $L$ : total active length of column

If several shorter separation units are combined and connected in series, the dead volumes and, possibly, proper exchange resistances between adjacent units have to be taken into account by means of appropriate juncture conditions (compare Erlenkeuser, 1973a). The role of dead volumes on run-time and optimum working conditions appears of secondary importance and will not be treated here in detail. As an example, these effects are briefly demonstrated in figure 4.

The quasi-linear partial differential eq (2.3) must be solved numerically by means of a finite difference scheme (Erlenkeuser, 1973a), if the calculations are to be of the same accuracy as the measurements obtained

with carefully constructed separation columns. On the other hand, several authors (Pak, ms; Felber and Pak, 1973; Kretner, ms; Kretner and Dickel, 1975; Grootes and others, 1975; Grootes, ms) report good agreement between measurements and an approximate model which describes the variation of the concentration with time by a single exponential term and one relaxation time only. A simple yet sufficiently precise model is of great interest with respect to the determination of the optimum operating conditions of the enrichment plant. It would greatly simplify the calculations and save computer time, thus allowing a more detailed investigation of the optimum working conditions with respect to run-time, total sample amount, and running costs.

Such a model has been presented by Kretner and Dickel (1975). Their model, however, neglects the isotope mass accumulated in the column itself, and this violation of the mass conservation law results in intolerably large errors under optimum working conditions at high isotope yield. Therefore, we derived another, more suitable approximative description of the enrichment process. This model was checked against the numerical solution of (2.1) and then applied to the optimization problem.

Recently, we became aware of the work of Felber and Pak (1974), who have anticipated many of the basic ideas also used in our model. However, the actual model these authors present was derived in a different way, and its accuracy suffers from an asymmetry concerning the role of the reservoirs at the column ends as compared to the amount of isotope in the column itself (compare eq 2.13).

The transport equation (2.1) is most easily solved if transport  $\tau$  is assumed to be independent on the column coordinate  $z$ , that is,  $\tau_z = \partial\tau/\partial z = 0$  (Fleischmann and Jensen, 1942). Strictly speaking, this assumption holds true only for the final equilibrium state and means that no isotope is being accumulated in the column itself (compare eq 2.2). Clearly, for the non-stationary state, this approximation is invalid on the long-term scale, particularly under optimum operating conditions when the positive sampling reservoir is almost negligible and a considerable amount of the isotope will be accumulated in the column. On a short-term scale, however, and under suitable boundary conditions, the enrichment process may be considered a series of consecutive stationary states, each of which accumulates a negligible amount of isotope in the column itself, while the overall accumulation is controlled by the mass conservation law.  $\tau_z = 0$ , then, may indeed provide a reasonably good presumption to start with.

This view appears particularly good in the case a sampling bulb is used, even a small one. The longitudinal gradient  $\tau_z$  of the isotope transport and the rate of the simultaneous build-up of the concentration gradient are effectively determined by the boundary conditions. With the column end closed, the isotope carried along from the inner parts of the separation tube causes a rapid rise of concentration in an initially

infinitely small volume at the very end of the separation tube (compare boundary conditions (2.5) with  $M_+ = 0$ ). If, on the other hand, the column feeds into a reservoir, the isotope concentration at the column end increases at a much slower rate, and the feedback on the transport  $\tau$  and its variation with  $z$  is greatly reduced. With  $\tau_z = 0$  and  $c \ll 1$ , eq (2.1) is solved by

$$c = \frac{\tau}{H} + \left( c_- - \frac{\tau}{H} \right) e^{2A z} \quad (2.6)$$

$$2A = H/K$$

Since the presumption  $\tau_z = 0$  violates the equation of continuity (2.2), the mass conservation must be used explicitly in the integral form

$$M_- c_- + \mu \int_0^L c(z) dz + M_+ c_+ = M_0 c_0 \quad (2.7)$$

where

$M_0$ : total working mass

Combining (2.6) and (2.7) we obtain

$$-\frac{\tau}{H} A_1 + c_- (1 + A_1) = c_0 \quad (2.8)$$

$$A_1 = \left( \frac{M_+}{M_0} + \frac{M_s}{M_0} \frac{1}{2A L} \right) (e^{2A L} - 1) - \frac{M_s}{M_0}$$

where

$M_s = \mu \cdot L$  mass of gas in the separation tube

The variation of the transport  $\tau$  with time may now be derived by the aid of boundary conditions (2.5). Differentiating (2.6) with respect to time  $t$ , substituting  $z = L$ , and inserting (2.5) yields a simple ordinary differential equation which is solved by

$$\tau = H c_0 e^{-t/\theta} \quad (2.9)$$

$$\theta = \theta_1 = \frac{1}{H} \frac{e^{2A L} - 1}{\frac{1}{M_+} + \frac{1}{M_-} e^{2A L}}$$

where

$\tau(t=0) = H \cdot c_0$  is the initial transport as given by (2.1) with  $c_z(t=0) = 0$  and  $c(t=0) = c_0$ .

As a result of this strict mathematical treatment, the accumulation of the isotope in the column itself is reflected in the term  $A_1$  only and does not enter the time scale parameter itself, which, for this solution, depends on the size of the reservoirs alone. From the physical point of view, however, this feature must be considered too strong a simplification, in particular for columns with small sampling bulbs as used under opti-

imum operating conditions. A better approximation may be achieved considering the isotope transport through the column cross section at the neutral point  $z_0$ , that is the point where the concentration at time  $t$  is the same as the initial one. For a concentration profile of the type as represented by eq (2.6),  $z_0$  is found independent on time  $t$ .

$$z_0 = \frac{1}{2A} \ln(1 + A_1) \quad (2.10)$$

The isotope transport  $\tau'$  at  $z_0$  is given by the rate of the isotope depletion below or enrichment above.

$$\begin{aligned} \tau' &= - \frac{d}{dt} \left\{ M_- c_- + \mu \int_0^{z_0} c(z) dz \right\} \\ &= \frac{d}{dt} \left\{ M_+ c_+ + \mu \int_{z_0}^L c(z) dz \right\} \end{aligned} \quad (2.11)$$

$\tau'$  appears to represent better the average transport along the column than does the transport given by the boundary conditions (2.5). Thus, we will assume  $\tau = \tau'$ . Evaluating (2.11) by the aid of (2.6) and (2.10), a second relation between  $\tau$  and  $c_-$  emerges in addition to eq (2.8):

$$\tau = - \left\{ M_- + \frac{M_s}{2A L} A_1 \right\} \frac{dc_-}{dt} + \frac{1}{H} \frac{M_s}{2A L} \left\{ A_1 - \ln(1 + A_1) \right\} \frac{d\tau}{dt} \quad (2.12)$$

Substituting  $dc_-/dt$  by means of (2.8) a simple differential equation is obtained providing a solution analog to (2.9) with

$$\theta = \theta_2 = \frac{1}{H} \cdot \left\{ \frac{A_1}{1+A_1} M_- + \frac{\mu}{2A} \left( \ln(1 + A_1) - \frac{A_1}{1+A_1} \right) \right\} \quad (2.13)$$

Deleting the second term in the curled brackets provides the model of Felber and Pak (1974).

Combining (2.6), (2.8), and (2.9) one obtains the concentration  $c$  as

$$\frac{c}{c_0} = e^{-t/\theta} + \frac{1 - e^{-t/\theta}}{1 + A_1} e^{2A z} \quad (2.14)$$

$A_1$  is related to the equilibrium enrichment factor  $m_{+eq}$  according to

$$m_{+eq} = \frac{c_+(t=\infty)}{c_0} = \frac{e^{2A L}}{1 + A_1} \quad (2.15)$$

Another quantity often used is the equilibrium separation factor  $q_{eq}$  which is given for  $c \ll 1$  by

$$q_{eq} = \frac{c_+(t=\infty)}{c_-(t=\infty)} = e^{2A L} \quad (2.16)$$

Eq (2.14) fulfills the mass conservation law (2.8) regardless the functional form of  $\theta$ .

Finally, the enrichment factor  $\bar{m}_+$  is to be calculated of an enriched sample of mass  $M_{\text{ex}}$ , one part of which is withdrawn from the sampling section of the separation tube, while the other is collected in the positive sampling reservoir.

$$\bar{m}_+ = \frac{\mu \int_{L-\Delta}^L c(z) dz + M_+ c_+}{M_{\text{ex}} c_0} \quad (2.17)$$

$$= e^{-t/\theta} + \frac{1}{M_{\text{ex}}} \left( M_+ + M_- \frac{1 - e^{-2A\Delta}}{2A L} \right) \frac{1 - e^{-t/\theta}}{1 + A_1} e^{2A L}$$

where

$$\Delta = \text{length of sampling section; } 0 \leq \Delta \leq L$$

The run-time  $t_m$  up to a given enrichment factor  $\bar{m}_+$  follows from

$$e^{-t_m/\theta} = 1 + \frac{M_{\text{ex}} (\bar{m}_+ - 1)}{M_{\text{ex}} + \frac{M_s}{2A L} (1 - e^{-2A\Delta} - 2A\Delta)} e^{2A L} - \frac{1 + A_1}{M_{\text{ex}}} \quad (2.18)$$

where  $M_{\text{ex}} = M_+ + M_s \cdot \Delta/L$  and  $M_+, \Delta \geq 0$ . Note that  $t_m$  may become imaginary if the operating conditions are such that the isotope amount preassigned,  $M_{\text{ex}} \cdot \bar{m}_+$ , cannot be accumulated because either the column is too short and/or the total working mass of gas is too low.

#### COMPARISON OF THE APPROXIMATE MODEL WITH THE NUMERICAL SOLUTION

The accuracy of the approximate model derived above has been checked against the numerical solution of the separation tube eq (2.3). As shown elsewhere (Erlenkeuser, 1971a and ms, 1973a; Henseler, ms, 1977), the numerical solution provides an excellent description of the temporal behavior of the isotope enrichment at the different stages of the column, with an accuracy generally better than 1 percent of the isotope concentration, and may therefore serve as a reference for the model developed here, not only from the mathematical point of view but also with respect to the relevance of the approximate solution as to reality. The neglect of the  $^{13}\text{CH}_4$  species in the following discussion is not thought to affect severely this latter point.

Both models were compared for operating conditions as of interest with respect to the radiocarbon dating method. According to the physical processes in the thermal diffusion column, the disagreement between these differently calculated enrichment factors should be greatest at the positive column end with no sampling bulb being attached. The accuracy

check has been based on this worst case in order to provide an upper limit of the error of the approximate model.

Identical boundary conditions were used, and equal numerical values were assigned to the different parameters for both computations. Since the numerical model makes no allowance for the  $^{13}\text{CH}_4$  component, the numerical solution, which is valid for a ternary mixture of  $^{12}\text{CH}_4$ ,  $^{13}\text{CH}_4$ , and  $^{14}\text{CH}_4$ , was based on a negligibly small initial concentration of the intermediate molecule of  $10^{-4}$ , which no longer affects the  $^{14}\text{C}$  enrichment. The calculations further assume a column without internal dead volumes.

The nature of the deviation of the approximate model from the numerical solution is illustrated by figure 1. Curves D and E (ordinate

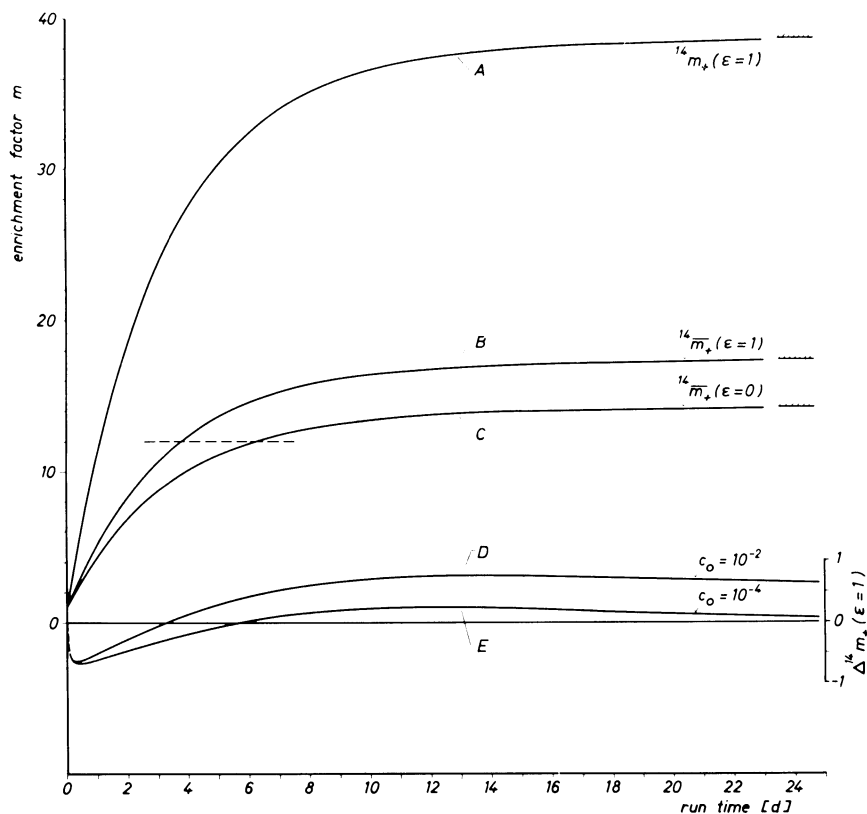


Fig. 1. Variation of different enrichment factors (curves A, B, C) and of the error of the approximate model (curves D, E) with time.

A:  $^{14}\text{C}$  enrichment at the positive column end without sampling bulb

B:  $^{14}\text{C}$  enrichment averaged over the sampling section of the column

C:  $^{14}\text{C}$  enrichment in the sampling bulb

D, E: Deviation of the approximate model from the numerical solution, calculated for two concentrations of the intermediate molecule  $^{13}\text{CH}_4$  (Enriched sample:  $1.8\text{g} \times 12$ , total mass of gas: 40g, column length: 10m, operating pressure: 1.4 atm).



scale at the right) show a temporal variation of the difference  $\Delta^{14}\text{m}_+$  of the  $^{14}\text{CH}_4$  enrichment factors at the positive column end as calculated from both methods. The enrichment factor itself is given in curve A, which represents the numerical solution. As suggested by the basic assumptions underlying the approximate model, the initial rapid rise of the isotope concentration particularly at the closed end of the column cannot be followed by the model. This is indicated by the rapidly growing deviation toward negative values (curve E). The strong isotope accumulation at the beginning, however, results in relatively steep concentration gradients, which in turn reduce the isotope transport during the later periods of time (compare eq 2.1) as compared to the approximate model which just neglects this relationship. As a consequence, the numerical solution is overtaken by the approximate model, and the deviation  $\Delta^{14}\text{m}_+$  becomes progressively positive, until the mass conservation law forces both models to approach equal enrichment factors in the final equilibrium state.

The approximate model has been checked in the way just outlined for 64 working conditions that were different with respect to total working mass (grid points investigated: 24, 40, 60, 80 g), column length (6, 10, 14, 18 m), and working pressure (0.8, 1.2, 1.4, 1.8 atm), while the geometry of the column cross section and the working temperatures were not varied (table 1). Maximum isotope separation in the equilibrium state is obtained at 0.925 atm.

The greatest positive errors occur under conditions when the isotope mass in the negative reservoir will not be seriously depleted during the enrichment process, that is, for short columns, high total working mass, and intermediate pressures not too much different from the equilibrium state optimum value. The relative maximum error never exceeded +0.74 percent. It is systematically greater, however, if the proper initial concentration of the intermediate molecule,  $^{13}\text{CH}_4$ , is taken into account (fig. 1, curve D). This effect results from the non-linear term  $H c (1-c)$  in transport eq (2.1) indicating  $H (1-c)$  to be the effective transport coefficient rather than  $H$  itself.

TABLE I

## Fixed parameters of the thermal diffusion column

Cross-section parameters	
Hot wall radius	: 2.0 cm
Cold wall radius	: 2.6 cm
Hot wall temperature	: 400°C
Cold wall temperature	: 14°C
Column transport coefficients ( $^{14}\text{CH}_4$ - $^{13}\text{CH}_4$ )	
$H^*$ ( $H = H^* p^2$ )	: $4.4_{10^{-3}}$ g/s atm <sup>2</sup>
$K^*_c$ ( $K_c = K^*_c p^4$ )	: $2.6_{10^{-3}}$ g cm/s atm <sup>4</sup>
$K_d$	: $1.9_{10^{-3}}$ g cm/s
$K = K_c + K_d$	

More dramatic errors occur during the initial stage. The relative maximum errors may amount to  $-10$  percent for both  $^{13}\text{CH}_4$  and  $^{14}\text{CH}_4$  and are greatest when the negative reservoir is small and becomes rapidly depleted (long columns, small total working mass).

The above discussion refers to the isotope enrichment in an infinitely small mass of gas at the positive column end. Considering the integral enrichment averaged over the sampling section of the column, the relative error of the approximate model appears smaller in most cases studied but still is of the same order of magnitude. The negative error stage — the analogue to that shown in figure 1 — may extend nearly up to the equilibrium state and thus may introduce considerable error in the later period of the enrichment process. The errors observed were generally between 0 and  $-5$  percent and never beyond  $-10$  percent (initial  $^{13}\text{CH}_4$  concentration:  $10^{-4}$ ). The positive errors in the late stages of the enrichment process were about  $+1$  percent or less.

Similarly, the accuracy of the approximate model is not much better, if the column feeds into a sampling bulb of relatively low mass content as favored in the present context (see chap. IV). Of course, the sampling bulb greatly reduces the initial growth rate of the isotope concentration but has little effect on the transport phenomena later on, which are based on increasingly longer time scales. The latter is the result of the continuously growing fraction of the amount of gas in the separation tube becoming involved in the isotope accumulation process as it proceeds from the ends of the column toward the inner parts.

Thus, the accuracy of the approximate model under the conditions studied here appears insufficient for analytical purposes. Fortunately, however, the errors proved small enough and the rate of the isotope enrichment with time sufficiently high in most cases to provide run-time figures of reasonably good accuracy and thus make the model a useful tool for solving optimization problems. In 70 percent of the conditions studied, the run times were found to be correct within two tenths of a day, with an absolute range between 2.5 and 21 d (enriched sample:  $1.8 \text{ g} \times 12$  from column). More erroneous figures, generally too high, were found for long columns and small total working mass, when the column must be driven very close to equilibrium in order to achieve the enrichment factor wanted. Under these conditions, even small differences in the enrichment factors produce large errors in time, due to the extremely low slope of the enrichment versus time curves.

Although these results question the general value of approximate models of this simple type as studied here, they do not seriously affect their usefulness in optimization studies.

#### MINIMUM RUN-TIME CONDITIONS

Thermal diffusion columns for  $^{14}\text{C}$  enrichment have been successfully operated on carbon monoxide and methane. From our view (Erlenkeuser, 1976) the latter gas appears the more convenient medium, since it is easily prepared from the radiocarbon sample, is not corrosive, can

easily be handled in the vacuum system of the enrichment plant, and can be readily analyzed for stable carbon and radiocarbon isotopes without further treatment. The following discussion is therefore confined to methane.

The run-time after which a given amount of sample gas will be found enriched by a given factor is dependent on the geometry of the separation plant, that is the width of the separation gap, the circumference of the hot tube, and the length of the separation column as well as the size and levels of the different storage, dead, and sampling volumes, and further depends on the operating conditions, that is the hot and cold wall temperatures and the working pressure. There is a complex interference of all these parameters, and the numerical evaluation of the enrichment model, even of such a simple one as derived above, can only be done by computer.

We have discussed elsewhere (Erlenkeuser, 1976) that with methane as the working gas the hot wall temperature should be as high as the thermal stability of the molecule will allow. A temperature of  $400^\circ\text{C}$  ( $673^\circ\text{K}$ ) appears suitable.

The width of the separation gap has a very pronounced influence on the working pressures and run-times. Although smaller gaps provide lower run-times (Erlenkeuser, 1976) problems will increase rapidly concerning the mechanical precision of the separation tube construction and, in routine work at laboratory conditions, the handling of gas pressures significantly above normal. Therefore, we have restricted the present study to a gap width of 6 mm which leads to working pressures in the range of 1 to 2 atm. The different parameters of the column cross section as used for the present calculations are compiled in table I and are not subjected to further discussion. The transport coefficients H and K have been derived from column experiments (Erlenkeuser, 1971a, b, 1973b).

Once the configuration of the column cross section has been selected, the working pressure affects both the distribution of the operating mass within the enrichment plant and the numerical values of the column transport coefficients H and K. As a result, the rate of the isotope enrichment is most effectively controlled by the gas pressure, and a pronounced run-time minimum can be established with respect to this parameter. This is demonstrated in figure 2 for a column 10 m long for different amounts of working gas and size of the enriched sample.

The run time is further affected by the allotment of the sample gas to be enriched to the different sampling volumes: one part, the fraction  $\epsilon$ , may be withdrawn from the sampling section of the separation tube, while the other fraction,  $1 - \epsilon$ , will be collected in the positive reservoir. The comparatively high run-times found for small  $\epsilon$  (fig 2) reflect the large amount of isotope to accumulate in the sampling bulb. As a consequence, the reservoir at the negative column end becomes far more depleted, the equilibrium enrichment factor is reduced, and the separation process must approach the equilibrium state more closely in order to achieve the enrichment factor required. This situation is illustrated

in figure 1, curves B and C. With  $\epsilon = 1$ , on the other hand, a higher isotope concentration must be attained at the column end in order to obtain an integral enrichment factor over the sampling section as desired. The latter mode of operation proves the more opportune (Erlenkeuser, 1976). Upon closer inspection, a compromise is found at  $\epsilon$ -values about 0.7 to 0.9. In most cases, however, the minimum is flat, and run-times at optimum  $\epsilon$  are hardly lower than at  $\epsilon = 1$  (fig 2).

The influence of the working pressure  $p$  and the column extracted sample mass fraction  $\epsilon$  on the enrichment time is illustrated in figure 2. The absolute minima as calculated from the approximate model (eq 2.18) are given by the asterisks and have been verified by the numerical solution (solid circles). Under certain conditions, such as high pressure and large sampling bulb ( $\epsilon \approx 0$ ), the finite total amount of isotope and the limited separation power of the column do not allow the isotope to become concentrated by the preassigned factor.

In order to illustrate what run-times may be obtained at best, they have been minimized as to both working pressure and sample mass fraction  $\epsilon$  and have been compiled in figure 3A in relation to the total working mass of gas for different amounts and enrichment factors of the extracted sample. All solid lines refer to a separation tube length of 10 m. Additional calculations were performed for tubes of 8, 12, 14, 16, and 18

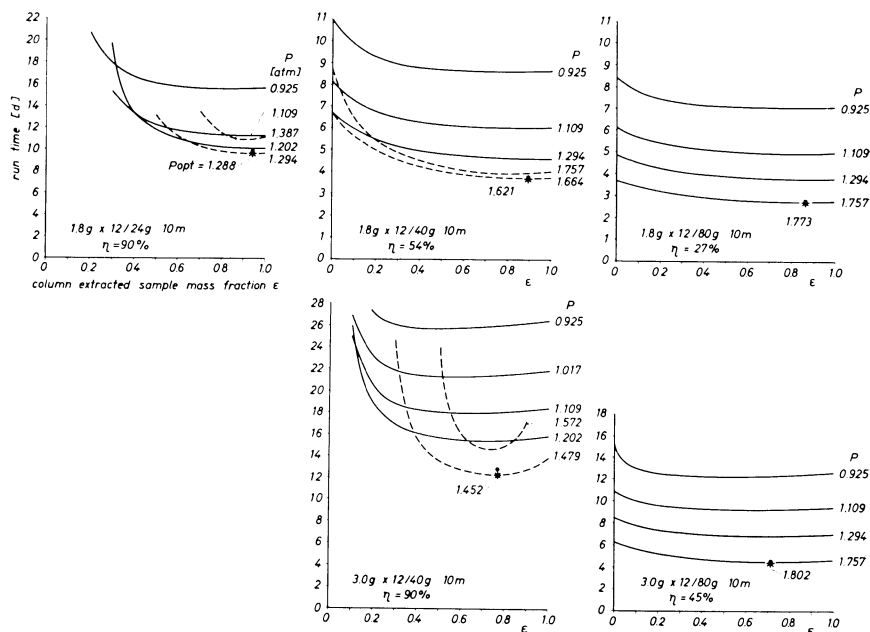


Fig. 2. The effect of working pressure and enriched sample mass fractions collected in the column itself on run-time. (Parameters given at the base of each sub-figure: mass of the enriched sample, enrichment factor, total working mass of gas, column length;  $\eta$  = isotope yield.)

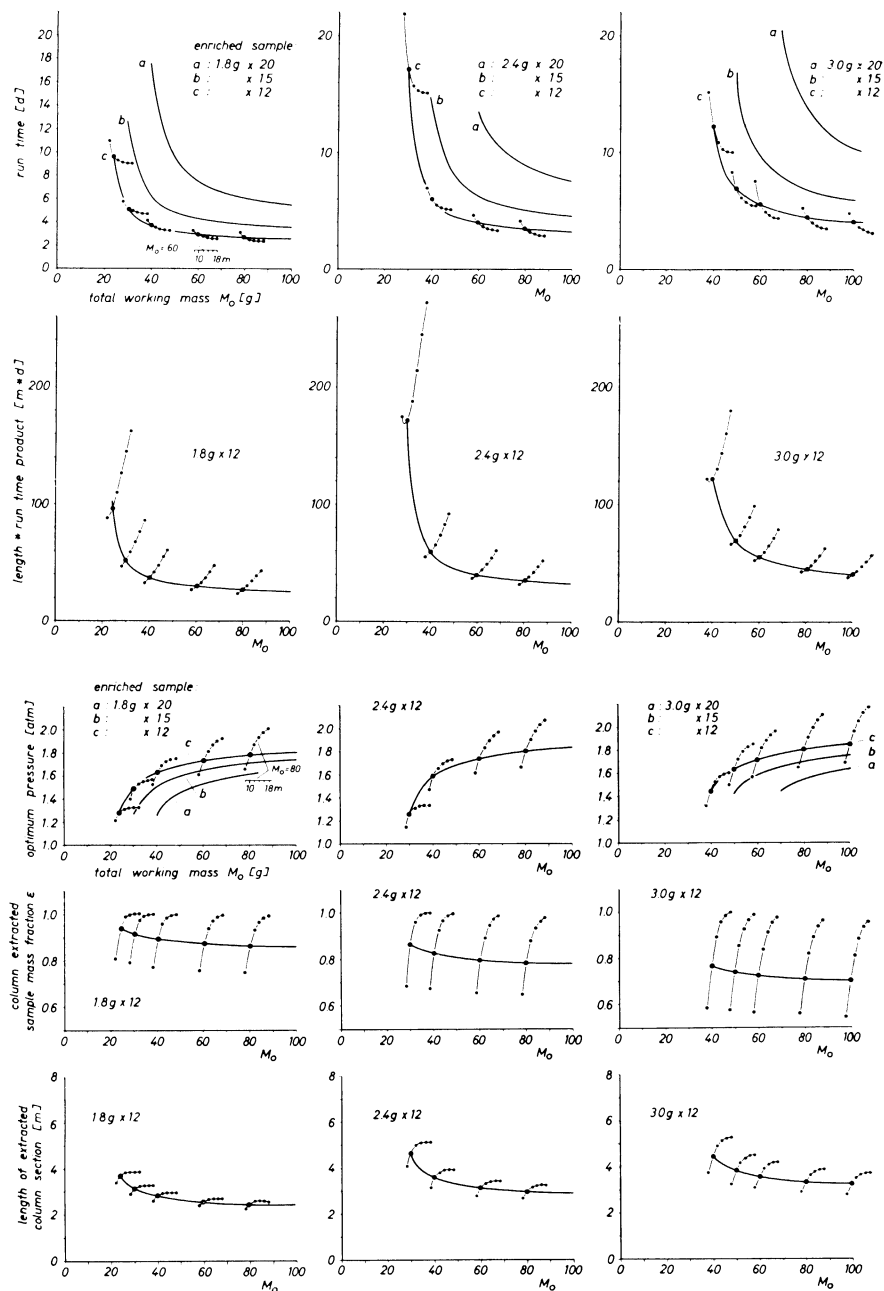


Fig. 3. Optimum operating conditions versus total working mass. (A) Run-time at optimum pressure and column extracted sample mass fraction  $\epsilon$ , and length—run-time—product; (B) Optimum working pressure, optimum column extracted sample mass fraction  $\epsilon$ , and optimum length of the sampling section.

m of length. These results are given by the dash-dot curves. The presentation is such that the dots proceed with column length from the left to the right, and each track relates to one single working mass  $m_0$  which is the one indicated on the x-axis by the 10 m dot.

The results show that the amount and the isotope concentration of the enriched sample as required for the purpose of radiocarbon dating may be obtained within a few days. The run-time is smaller the greater the initial amount of the isotope.

The optimum enrichment pressures (fig 3B) are between 1 and 2 atm. They are generally higher than the maximum separation pressure in the equilibrium state (0.925 atm) which they approach, however, when the negative reservoir becomes strongly depleted, and high separation factors must be attained in order to achieve the enrichment preassigned.

The column extracted sample mass fraction  $\epsilon$  is found close to 1 (fig 3B), in particular for small gas samples withdrawn. On the other hand, if greater sample amounts are needed, the use of a slightly greater positive reservoir appears more opportune. The actual sampling sections are about 2.5 to 5 m long (fig 3B). Reminding the flatly shaped minimum of run-time with respect to  $\epsilon$ , the length of the sampling section does not seem critical for many of the conditions of practical interest, and a section of fixed length, such as one separation unit of, say, 2.5 to 3 m, may be used throughout without appreciable loss of time.

Run-time may be further reduced by increasing the length of the separation tube (fig 3A). However, since the isotope transport along the column is determined by the cross-section data rather than by the length of the column, a noticeable gain is obtained at high isotope yield only, as due to the increased separation power (eq 2.16) which allows the enrichment process to be finished well before the equilibrium state has been approached too closely.

On the other hand, the operating costs, which may be taken proportional to the length-run-time-product, will strongly increase with column length. Henseler (1977) reports an electric power consumption of 5.6 watt per cm column length at 350°C hot wall temperature and a total cooling water flow of 650 l/h to give an average cold wall temperature of 14°C (10m column, 4 units, cooled in parallel). According to the numerical results shown in figure 3A, a column length of 10 m appears an agreeable compromise, which keeps operating costs low and simultaneously allows the desired amount of isotope to be collected within a convenient period of time. The run-times calculated above are minimum figures which do not take into account the dead volumes arising if several separation units of shorter length are arranged in series to form the actual column. Dead volumes at the ends of each unit cannot be avoided for constructional reasons and are introduced by the thermal convection loops which provide the gas exchange between consecutive units.

The approximate model has been extended to include the dead volumes at the corresponding level of the column and has been applied

to a four stage column of 10 m total length enclosing three dead volumes, 0.4 l each (for comparison: volume of one unit: 2.2 l). The column sampling length was kept constant at 2.5 m, that is the length of one unit, while the working pressure was optimized to yield minimum run-time. In general, the run-times calculated came out higher by about 0.5 d as compared to the former results shown in figure 3A. The effect of dead volumes — and of the non-optimal sampling length — becomes more pronounced at high isotopic yield and under near-equilibrium conditions. For example, run-time increased from 9.6 to 12.4 d for a sample of 1.8 g, 12-fold enriched, out of a total working mass of 24 g. With dead volumes included, the optimum working pressures are lower by a few tenth of an atm than those given in figure 3B. Another example of the effects of dead volumes is shown in figure 4C.

As a result, it appears from the calculations presented that the enrichment of  $^{14}\text{C}$  by thermal diffusion is a sufficiently fast and low sample mass consuming method to be used in routine radiocarbon dating work.

#### MEASUREMENTS

The results presented above are not directly supported by measurements as one might wish in regard to the surprisingly short run-times predicted by theory. Indirect support is given by the fact, that the essential parameters not known a priori, that is the column transport coefficients, have been determined from careful column experiments. These were run at comparatively low enrichment factors, however, so that their use for predicting the behavior of the column at a higher state of enrichment might be questioned. Thus, further experimental results, even if not gained at optimum conditions, would greatly help to elucidate the relevance of the theoretical calculations.

Due to the lack of our own measurements, published data were analyzed on the basis of the model presented here. Radii and length of the separation tubes and the amount of the final gas sample and its enrichment factor were taken from the literature. The column transport coefficients, however, have been derived by a least square fit of the present approximate model to the experimental results, inserting the geometrical configuration of the column and the experimental conditions as given by the authors. The numerical values of these coefficients are closely bound to the model used in the fit and may not compare with the authors' estimates obtained on a different way. They may be affected additionally by small dead volumes not mentioned by the authors or by slightly different working conditions of the enrichment units combined in the column. Hence, the optimum conditions shown in figure 4 should be regarded as qualitative rather than quantitative results. The data used for the optimization calculations are compiled in table 2.

Felber and Pak (1973) have established a short column, 4 m long, consisting of two shorter elements; the narrow separation gap (width: 3 mm) provides a comparatively high separation power. The enriched sample is taken from a positive reservoir.

TABLE 2  
Parameters of thermal diffusion  $^{14}\text{C}$  enrichment experiments by different authors and column transport coefficients underlying figure 4

	Felber and Pak (1973)	Kretner (1973)	Henseler (1977)
<b>Column dimensions</b>			
Hot wall radius	$R_H$ (cm)	2.25	2.0
Cold wall radius	$R_K$ (cm)	2.75	2.6
Total column length	$L$ (cm)	1079***	$4 \times 254.5\ddagger$
Neg. reservoir	$V_-$ (l)	250 at 19°C	85 at 22°C
Pos. reservoir	$V_+$ (l)	2.0 at 19°C	0
<b>Operating conditions*</b>			
Hot wall temp.	$T_H$ (°C)	309	334
Cold wall temp.	$T_K$ (°C)	19	14
Pressure	$p$ (atm)	0.967	1.00
<b>Experimental results</b>			
Enriched sample size		$2.52\text{g} \times 14.4$	$2.47\text{g} \times 10.6$
Collection mode		pos. bulb	col. 3 + col. 4†
Run-time	(d)	15	11
<b>Transport coefficients used for calculation</b>			
$H^*$	( $\text{g s}^{-1} \text{atm}^{-2}$ )	2.22 $10^{-6}$	2.32 $10^{-5}$
$K^*_c$	( $\text{g cm s}^{-1} \text{atm}^{-1}$ )	8.31 $10^{-6}$	5.14 $10^{-3}$
$K_d$	( $\text{g cm s}^{-1}$ )	0.7 $10^{-3}$	1.7 $10^{-3}$

\* Working gas:  $\text{C}_2\text{H}_2$ ; \*\* Intermediate dead volumes not known; \*\*\* No intermediate dead volumes; † Succession of separation units and dead volumes (in  $\text{cm}^3$  at 22°C):

$V_-$ , col. 1, 462, col. 2, 216, {246, col. 3, 216, [269, col. 4, 69],  $V_+$ }

In curled brackets: part from which enriched gas was sampled in the experiment

In square brackets: sampling configuration for curves A, A' in figure 4C.

curve

--- A --- B --- C ---

2.32  $10^{-5}$  2.32  $10^{-5}$  2.32  $10^{-5}$

5.14  $10^{-3}$  5.14  $10^{-3}$  2.6  $10^{-3}$

1.7  $10^{-3}$  1.7  $10^{-3}$  1.7  $10^{-3}$

1.3g  $\times$  12 pos. bulb 17.2

2.22  $10^{-6}$  8.31  $10^{-6}$  0.7  $10^{-3}$

( $\text{g s}^{-1} \text{atm}^{-2}$ ) ( $\text{g cm s}^{-1} \text{atm}^{-1}$ ) ( $\text{g cm s}^{-1}$ )

(d)

( $\text{g cm s}^{-1}$ )

( $\text{g cm s}^{-1} \text{atm}^{-1}$ )

( $\text{g s}^{-1} \text{atm}^{-2}$ )

( $\text{g cm s}^{-1}$ )



The column transport coefficients  $H$ ,  $K$  have been determined as mentioned above.  $K_c$  was obtained from  $K$ , subtracting  $K_a$  as calculated by the authors:  $K_a$  is known to be little affected by constructional inadequacies and may be calculated from the working gas transport properties with good reliability.

The experimental result of Felber and Pak is indicated by the open circle in figure 4A. Increasing the working pressure and making use of the column itself for sample gas collection would have lowered the run-time markedly (fig 4A, curve A, at optimum pressure and collection mode conditions). Apparently, however, the column is driven rather close to the equilibrium state. An appreciable reduction of run-time will result from increasing the length of the column (curves B, C, optimum conditions). The run-times, then, are of the same magnitude as calculated earlier (fig 3A), for almost the same size of the enriched sample ( $2.4 \text{ g} \times 15$ ).

Kretner (1973) established a one-unit-column 10 long. He presents numerous measurements of the  $^{13}\text{C}$  enrichment at different operating pressures. However, a consistent set of the pressure reduced coefficients  $H^*$  and  $K_c^*$  ( $H = H^* p^2$ ,  $K = K_c^* p^4 + K_a$ ) equally valid for all pressures studied could not be derived from these results within acceptable limits of error, and no figure of  $K_a$  could be estimated from the variation of  $K$  with the operating pressure.  $K_a$ , therefore, had to be calculated theoretically from the gas transport properties. Furthermore, the rate of the  $^{14}\text{C}$  enrichment measured by Kretner appears very much slower than expected from the  $^{13}\text{C}$  isotope enrichment. This might be accounted for by the relatively large samples of highly enriched gas frequently withdrawn from the positive reservoir in order to measure in detail the progress of the  $^{14}\text{C}$  enrichment with time.

In view of the low reproducibility of the column coefficients as estimated by means of our model, minimum run times have been calculated both for the most favorable set of parameters derived from Kretner's  $^{13}\text{C}$  studies (fig 4B, curve C) and the worst case provided by the  $^{14}\text{C}$  measurements (curve B). For comparison, curve A; like curve B, for the most unfavorable case, illustrates the run-time at optimum size of the sampling reservoir, with the pressure kept constant as used by Kretner (table 2). In this latter case, run-times are not subjected to pressure dependent errors as otherwise might arise from systematically wrong estimates of the column coefficients. According to curve A, the run-time under Kretner's conditions (open circle) would reduce at optimum collection conditions by about 3 days.

The run-times shown in figure 4B are markedly higher also in the most favorable case (curve C) than calculated earlier (fig 3A) for an enriched sample of comparable size. As compared to a theoretical estimate the figure of  $K_c$  as used in table 2 appears very high and seems to reflect a large contribution of parasitic remixing effects in the column.

Henseler (1977) operated a 10 m thermal diffusion column consisting of four enrichment units, each 2.5 m long. The units are connected by

thermoconvection loops, which did not impede the isotope exchange between adjacent units in any way. Starting with 62g of methane, Henseler obtained a sample of 2.47g, 10.6 fold enriched within 11 days (fig 4C, open circle). No positive sampling bulb was used.

The different intermediate dead volumes (table 2) between the enrichment units have been taken into account in an appropriately modified version of our model. Effective transport coefficients, the same for all elements of the column, were introduced in order to make allowance for slightly different working temperatures of the four separation units. If adjusted to the  $^{13}\text{CH}_4$  enrichment, the model was found to meet the measured variation of this species with time on the different stages of the column, and the accuracy was satisfying also at the positive column end.

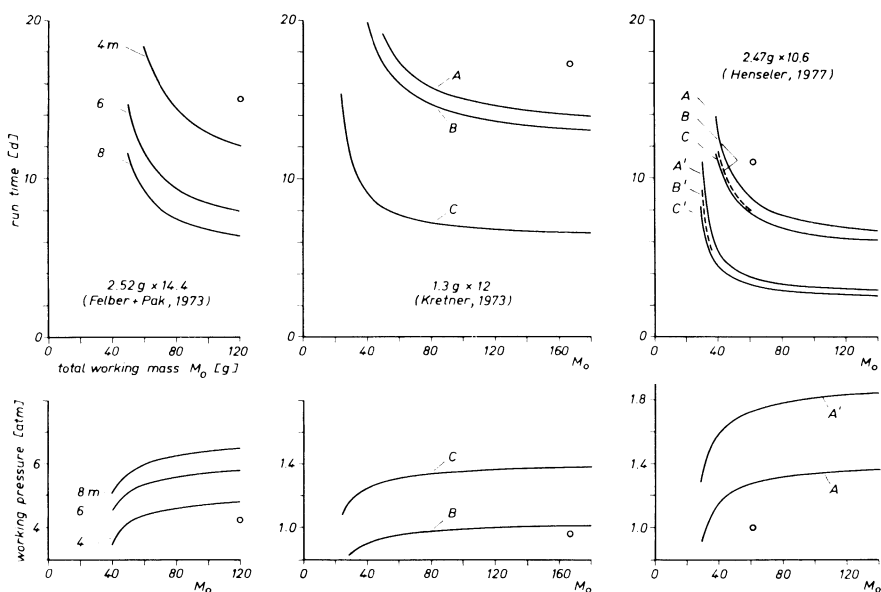


Fig. 4. Results of  $^{13}\text{C}$  enrichment experiments (o) as compared to theoretical prediction. (Size of enriched sample as specified; for details see text and table 2.)

A. Felber and Pak (1973): 4 m column with sampling bulb; curves represent optimum working pressure and sampling mode conditions for different column lengths.

B. Kretner (1973): 10.79 m column with sampling bulb.

A: 735 Torr working pressure; optimum sampling mode conditions.

B, C: Optimum working pressure and sampling mode conditions for extrema of remixing coefficient  $K^*$ , as obtained from re-evaluation of experiments.

C. Henseler (1977): 10.19 m 4-stage column; upper 2 columns for sample collection; no sampling bulb.

Curves: sample collected from upper column only; optimum working pressure conditions.

A, A': intermediate dead volumes included.

B, B': dead volumes set zero.

C, C': as B, B'; optimum working pressure and sample collection mode conditions.

(Parameters of A', B', C', as given in table 1.)

For collection of the enriched sample, Henseler combined the contents of the two upper separation units (table 2). This large sampling length (about 5m or half of the column length) keeps the average enrichment low and yields correspondingly long run-times. More favorable conditions are achieved if the sample collection is restricted to the upper tube, supplemented by an appropriately sized positive reservoir. Run-times obtained for these conditions at optimum working pressure are presented in curve A of figure 4C. If additionally the intermediate volumes are set to zero, run-times are lowered by another 0.5 to 1 day (curve B). No important further improvement is gained if the sampling section of the column is optimized (curve C). The optimum operating pressures for curves A, B, C are the same within a few tenths of an atm and are represented by one curve only (fig 4C, lower part).

For comparison the calculations were repeated using the column coefficients of table 1. The results are shown in figure 4C, curves A', B', C', which otherwise are equivalent to curves A, B, C, respectively. The very much lower run-times are the effect of the higher hot-wall temperature assumed in table 1, which not only increases the separation coefficient  $H^*$  but also yields a much lower remixing coefficient  $K^*_c$  (Erlenkeuser, 1976).

Henseler's experiments at least demonstrate that the enrichment of  $^{14}\text{C}$  for the purpose of radiocarbon dating may be performed in a comparatively short period of time and at good isotope yield. Moreover, his results are likely to become improved further by selecting more suitable experimental conditions.

The calculations were performed on the PDPI0 computer at the University of Kiel computer center.

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