

## Enrichment of Tritium by Thermal Diffusion and Measurement of Dated Antarctic Snow Samples

**Abstract.** A thermal diffusion column allows a recovery of  $99 \pm 1$  percent of the tritium originally contained in about 50 liters at standard temperature and pressure of hydrogen gas in a final volume of 3.8 liters over a 2-day period. After a tenfold enrichment by electrolysis, a tritium concentration of  $10^{-18}$  with an experimental error of a few percent may be measured with a low-level Geiger counter. The results on some well-dated Antarctic snow samples (between 1941 and 1953) are in general agreement with published data.

The radioactivity of tritium can be measured without isotopic enrichment (1) provided the ratio of the number of T atoms to the number of H atoms in the sample (usually water) is larger than  $T/H \approx 10^{-16}$ . But the concentrations are usually lower in natural water samples or samples produced by nuclear reactions in accelerator experiments. This necessitates the enrichment of the heavy isotope. The standard enrichment procedure is electrolysis (2) of the sample. If the tritium is enriched by a factor of  $10^3$ , about half of the tritium is lost with the escaping hydrogen gas. The determination of the tritium retention introduces an error of 10 percent or more (3).

To avoid this large error, Gonsior (4) used a continuous-flow thermal-diffusion column for hydrogen gas to concentrate the tritium (5). With the column dimensions suggested by Grove *et al.* (6) we have built such a column. Construction features and test measurements are reported here.

A different type of thermal diffusion column has been described by Verhagen and Sellschop (7).

If the electrolysis and thermal diffusion procedures are combined so as to electrolyze the water sample from 500 ml to 50 ml, convert it to hydrogen gas, and then concentrate the tritium in the column, tritium concentrations of the order of  $T/H = 10^{-18}$  can be measured with an error of 10 percent or better. By experiment,  $16 \pm 3$  percent of the tritium is lost under these conditions during the electrolysis stage and  $1 \pm 1$  percent in the thermal diffusion process.

The complete system is shown in Fig. 1. The water sample is reduced to  $H_2$ , with magnesium at  $500^\circ\text{C}$ . The hydrogen gas is then purified by passage through palladium metal (surface area,  $62.8\text{ cm}^2$ ; thickness,  $0.15\text{ mm}$ ). No isotopic fractionation occurs when the metal is maintained at more than  $400^\circ\text{C}$  (8). In order to produce an almost continuous gas flow, a Toepler pump transfers the gas into a 6-liter

bulb from which it enters the column through a length of capillary tubing.

The reduction apparatus is self-regulating; the temperature of the water sample and the frequency of the Toepler pump set the speed of the reduction process. Normally, 2 liters of  $H_2$  gas at standard temperature and pressure (STP) per hour are passed through the column.

The column dimensions are shown in Fig. 2. The length of  $L'$ , equal to 6.4 m, of the upper (derichment) part, is determined by the condition that a tritium concentration ratio  $c_i/c_f \approx 100$  can be realized for a hydrogen-gas flow rate  $V$  of less than 3.6 liter/hr. The length  $L$  of the enrichment part depends on the total amount of hydrogen gas to be processed. The 3.6-m column should be able to handle about 360 liters (STP) of sample gas if the flow is infinitely slow. With a finite flow, we have shown experimentally that the tritium of at least 50 liters (STP) of gas can be held in the column. Details of the design are given in the appendix.

The column is divided into four sections of 2.5 m each (see Fig. 1). The section walls are made of straight glass tubing and are cooled with tap water ( $290^\circ\text{K}$ ). The top of one section is

joined to the bottom of the next section through two thin glass tubes which are connected to opposite sides of the section ends. A small circulation pump provides a uniform tritium concentration within the circulation system. The vertical gas motion in the column prevents repeated circulation of the same portion of gas.

A platinum-iridium (80 percent Pt, 20 percent Ir) wire of 0.4 mm diameter is kept at the center of each section by about eight wire crosses and is stretched by an iron weight of 12 g, fixed to the lower end. During operation the wire is heated with d-c current to about  $1150^\circ\text{K}$ . The thermal expansion of the wire makes the iron dip into a mercury vessel; by buoyancy, enough weight is lost so that breakage does not occur.

The depleted hydrogen gas leaves the "upper" end of the column and passes a one-way mercury valve which prevents air from entering the column even if the inside pressure should drop below that of the atmosphere.

An additional section at the enrichment end of the column will increase the total hydrogen which can be processed. Adding another section to the derichment column will permit us, with fixed ratio of  $c_i$  to  $c_f$ , to increase the flow of hydrogen gas. Hence it is easy to improve the operational characteristics of the column.

In order to test the performance of the apparatus, we have investigated the following points, using a standard water sample with a ratio  $T/H = (9.49 \pm 0.2) \times 10^{-15}$ .

1) A search for fractionation of the H-isotopes during the reduction process or the passage through the palladium

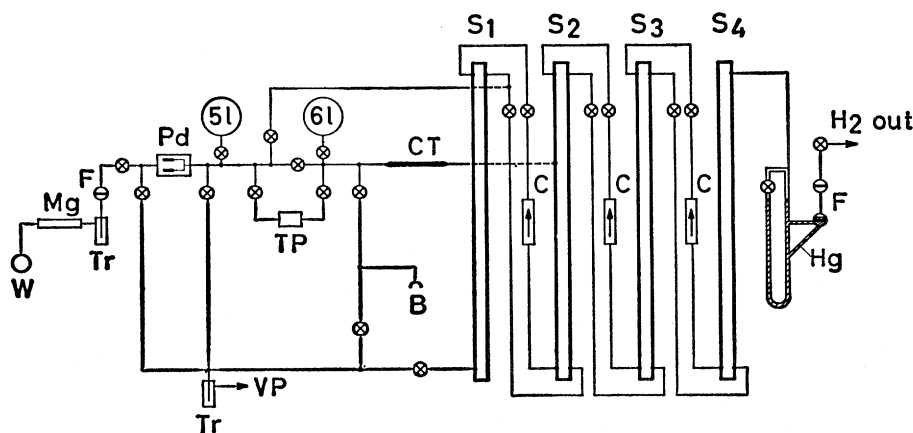


Fig. 1. Schematic diagram of reduction and thermal diffusion apparatus. W, water sample; Mg, magnesium reduction tube; Tr, liquid air trap; F, sintered glass disc; Pd, palladium leak; VP, vacuum pump; TP, Toepler pump; B, ball joint for counter connection; CT, capillary tubing; S<sub>1</sub>–S<sub>4</sub>, sections of thermal diffusion column; C, circulation pump; Hg, mercury.

Table 1. Tritium ( $H^3$ ) concentration of Antarctic firn samples. The probable year of precipitation is approximated to  $\pm 1$  year.

Enrichment factor		Measured H <sup>3</sup> (TU)	H <sup>3</sup> extrap- olated to year of precipitation (TU)
Electro- lytic	Thermal diffusion		
1941			
7.10	7.41	5.9	24.2
4.77	12.31	6.0	24.4
1948			
7.08	13.0	6.6	17.1
1952			
9.19	10.91	6.5	13.6
10.20	9.04	8.5	17.7
1953			
4.81	10.38	9.6	18.4
2.19	13.65	10.8	21.2

metal failed to show any such fractionation. Two conversions (without operation of the column) of the standard sample yielded T/H equal to  $(9.56 \pm 0.2) \times 10^{-15}$  and  $(9.54 \pm 0.2) \times 10^{-15}$ , with reduction efficiencies of 96 and 95 percent, respectively. Later improvements with the reduction procedure have made it possible to increase this efficiency to 100 percent. Repeated measurements to test the performance of the entire system (as shown below) indicate no errors due to isotopic fractionation.

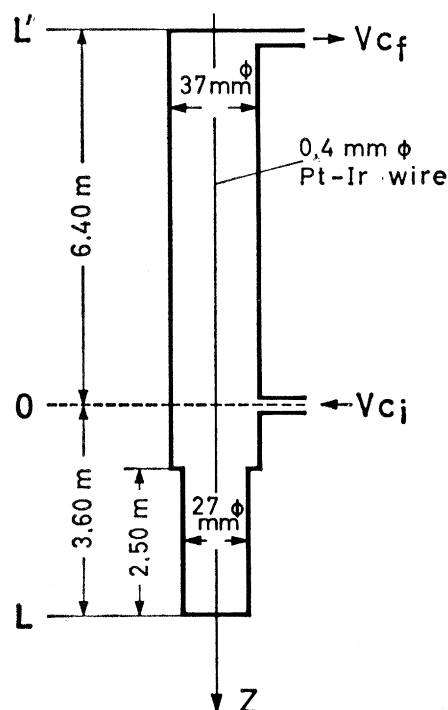


Fig. 2. Dimensions of the thermal diffusion column (schematically). Upper portion, derichment; lower portion, enrichment.

2) To verify the absence of "memory effects" in the system, we measured in direct sequence a sample of T/H  $\approx 8 \times 10^{-17}$  (measured twice), then the standard sample mentioned above, and then again the low-tritium sample. The results were  $(8.7 \pm 0.9) \times 10^{-17}$ ,  $(6.6 \pm 2.0) \times 10^{-17}$ ,  $(9.56 \pm 0.2) \times 10^{-15}$ , and  $(7.7 \pm 1.9) \times 10^{-17}$ . The data indicate the absence of noticeable memory effects.

3) The tritium separation was investigated as a function of time in the closed-off column (no gas flux through the upper part). The column was filled with the standard tritiated hydrogen gas to a pressure of 560 mm-Hg. With the center wire at 1150°K, the pressure rises to 760 mm-Hg. Figure 3 shows the fraction  $w_k$  of the total tritium contained in section  $k$ :

$$w_k = a_k v_k / \sum_{k=1}^4 a_k v_k$$

where  $a_k$  is the tritium counting rate and  $v_k$  the volume of the  $k$ th section, as a function of the separation time.

For  $t = 0$ , the curves do not start at the same point because the volumes of the sections are different. Since the radius of the first section is smaller than that of the others, the initial tritium transport from the second section into the first is smaller than from the third into the second, therefore the tritium content of the second section passes through a maximum. Sections four and three are practically free of tritium after 8 and 14 hours. After 12 hours 99 percent of the tritium is concentrated in the first two sections, and after about 20 hours in the first section.

Comparison of the amounts of tritium fed into the column before separation and removed afterwards indicates that no tritium is lost (or gained) during the operation.

4) If the column is operated with continuous hydrogen flow, it must run without flux for about 8 hours in order to remove the tritium from the last section. Then the gas flow is started.

The above-mentioned tritium standard sample was used at a flow rate of 2 liter/hr. In order to verify the expected enrichment  $c_i/c_f \approx 100$ , the gas leaving the upper end of the column was divided into four portions and examined for its tritium content. A total of  $1 \pm 1$  percent of the original tritium input activity was found. After about 20 hours, the conversion of the water sample was completed and the flow

ceased. The column was then operated for another 16 hours in the closed-off condition. Finally, the tritium content of each section was measured separately; 98.6 percent of the activity was found in the first section, 1.4 percent in the second, and none in the third and fourth sections. The activity totaled  $100 \pm 3$  percent of the tritium fed into the column. The data show that within a total operation time of 44 hours,  $99 \pm 1$  percent of the tritium originally contained in 36.7 ml of water can be recovered in about 3.8 liters of hydrogen gas, or  $97.6 \pm 1$  percent in 1.4 liters of hydrogen gas, ready for counting in a low-level gas counter.

An initial water sample of 500 ml, containing a T/H equal to  $1 \times 10^{-18}$  (designated 1 TU) will give rise to 0.74 count/min above background in our Oeschger-type counter (9) (effective to total volume ratio 0.24) if no tritium is lost during the combined electrolysis and thermal diffusion enrichment procedure. With a background of  $3.5 \pm 0.05$  count/min, this can be measured to within a statistical error of 10 percent in 1 day of counting time.

In collaboration with E. E. Picciotto, we have started a program to measure the tritium concentration of Antarctic firn along a profile in the ice shelf of King Baudouin Station (East Antarctica, 70°26'S, 24°19'E; average accumulation rate 40 cm of water per year). The age of the samples with respect to the time of deposition is known to  $\pm 1$  year by stratigraphy and by

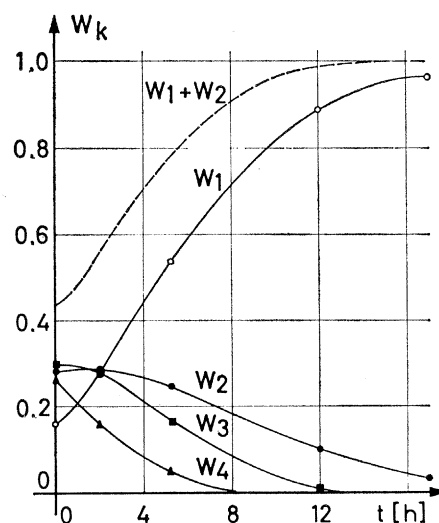


Fig. 3. Dependence of tritium separation on time (closed-off column, no gas flow).  $W_k$  is the fraction of total tritium in  $k$ th section.

variations in the oxygen isotope ratios (10).

The results of our measurements are listed in Table 1. For three of the four samples, independent double checks were performed to study the overall reproducibility of the technique. We conclude that measurements of this kind are reliable to within  $\pm 10$  percent if a starting sample volume of 500 ml is used. Further reduction of the error limit should be possible.

The few tritium data on Antarctic samples available from the work of Begemann and Libby (11) and Shen *et al.* (12) show that until 1955 the level was near 17 TU. Our data confirm this general statement concerning the tritium activity at this location prior to nuclear bomb explosions.

**Appendix.** Dimensioning of the column.

Furry and Jones (13) have derived the following expression for the mass transport  $t$  [g/sec] of the HT molecules:

$$t = H\bar{c} - (K_c + K_d)d\bar{c}/dz \quad (1)$$

$\bar{c}(z)$  is the average concentration of HT over the horizontal column cross section (number of HT molecules per total number of molecules) and  $z$  the coordinate shown in Fig. 2;  $H$ ,  $K_c$ , and  $K_d$  are functions of the inner radius  $r_c$  of the column, the wire radius  $r_w$ , the temperature  $T_w$  of the wire, the temperature  $T_c$  of the column wall, and the hydrogen-gas pressure. Grove *et al.* (6) have obtained experimental values of  $H$ ,  $K_c$ , and  $K_d$ , from which the functional dependence on the diameters and temperatures can be evaluated numerically.

When setting the dimensions of the upper (derichment) part of the column, the continuous flow of hydrogen gas must be considered. The net downward HT transport is given by the difference of the downward transport  $t/\rho$  [in  $\text{cm}^3$  of HT molecules/sec;  $\rho$  is the density of HT] by thermal diffusion, and the upward transport  $V\bar{c}$  resulting from the gas flow ( $V$ , flow rate in  $\text{cm}^3/\text{sec}$ ). In the stationary state one has

$$\frac{t}{\rho} - V\bar{c} = \text{constant} \\ \text{for } -L' \leq z \leq 0.$$

At  $z = -L'$ , the total transport must equal  $-c_f V$ , therefore

$$t = V\rho(\bar{c} - c_f). \quad (2)$$

If Eq. 2 is inserted into Eq. 1 and the

differential equation for  $\bar{c}$  is solved with the boundary condition  $\bar{c} = c_i$  at  $z = 0$ , the result is

$$\frac{c_i}{c_f} = \frac{H}{H - \rho V} \times \exp\left(\frac{H - \rho V L'}{K_c + K_d}\right) - \frac{V}{H - \rho V}$$

Numerical evaluation of this expression shows that, with  $V = 3.6$  liter/hr, the optimal column radius (14) is between 1.7 cm at  $T_w/T_c = 4$  [ $T$  in  $^\circ\text{K}$ ] and 1.9 cm at  $T_w/T_c = 2$ , and that with  $T_w/T_c = 3$ , one should obtain  $c_i/c_f = 100$  at about  $L' = 6$  m. We have chosen  $L' = 6.4$  m;  $r_w = 1.85$  cm; we expect  $c_i/c_f \geq 100$  for  $V < 3.6$  liter/hr and  $T_w > 1000^\circ\text{K}$ .

At  $z = 0$  the eigentransport  $t/\rho$  of the upper part of the column must equal the eigentransport of the lower part. Therefore the column diameter must not change at this point. This is accomplished by choosing the same diameter in the three "upper" column sections and inserting the sample gas in the middle of the second section (Fig. 1).

The radius of the lowest section has been selected in the following way: According to Eq. 1 the concentration will change with time until  $t = 0$ , and thereafter

$$\bar{c} = c_i \exp\left(\frac{Hz}{K_c + K_d}\right).$$

For a radius  $r_c = 1.35$  cm, the factor  $H/(K_c + K_d)$  has its maximum value, almost independently of the temperature ratio. A tube of this radius gives the shortest length  $L$ , and such was chosen for the first section.

H. V. BUTTLAR

B. WILK

*Institut für Technische Kernphysik  
der Technischen Hochschule,  
Darmstadt, Germany*

#### References and Notes

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5. It is an additional advantage of the thermal diffusion procedure that the sample is never in contact with the air or other sources of moisture so that tritium exchange with atmospheric water is avoided.
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14. Grove's work (6) indicates that, in the region  $60 \leq r_c/r_w \leq 100$ , the quantities  $H$ ,  $K_c$ , and  $K_d$  show almost no dependence on this ratio.
16. We thank Dr. E. E. Picciotto and Dr. W. De Brecuck for supplying the samples, Mrs. S. Wilgain for her help in the preparation of the samples, and Miss U. Schroer for her competent assistance in the laboratory. This work was sponsored by the Bundesministerium für wissenschaftliche Forschung.

6 July 1965

## Nuclear Mitochondria?

**Abstract.** *Recognizable mitochondria were detected in the nucleus of a leukemic cell. It is suggested that passage through enlarged nuclear pores, incorporation within a pinched off invagination, or inclusion within the nuclear envelope at telophase may have been responsible for this unusual event.*

During a study concerned with fine-structural aspects of the growth of ascites leukemia cells L 1210 in solid clumps in the abdominal cavity, the presence of a group of structures resembling mitochondria was observed within the nucleus (Fig. 1). One of these bodies (Fig. 2) could be definitely identified, on morphological grounds, as a mitochondrion, in that it showed a double outer membrane and internal cristae. A second body, which could be interpreted as an altered mitochondrion, was surrounded partially by a double membrane and contained what seemed to represent a remnant of cristae. The origin of several other vacuolar structures present in the same area could not be established.

In an attempt to explain such an unusual finding, we can suggest three possible mechanisms whereby these mitochondria may have been "trapped" within the nucleus. It is possible that one or more mitochondria may have "squeezed" through one of the enlarged pores present in the nuclear envelope of these leukemic cells. However, the passage of a particle the size of a mitochondrion through a nuclear pore seems most unlikely. The second possibility is that this unusual picture may represent a transverse section of cytoplasmic structures present in a nuclear invagination; these invaginations are very frequently observed in these cells. However, in all such cases the cytoplasmic structures apparently inside the nucleus appear surrounded by the