

LIQUID SCINTILLATION COUNTING METHOD OF NATURAL TRITIUM AND ITS APPLICATIONS TO HYDROLOGY AND METEOROLOGY

I. DOSTROVSKY, P. AVINUR AND A. NIR

Weizmann Institute of Science, Rehovoth

INTRODUCTION

THE assay of natural tritium has been of considerable interest in the last years, owing to the origin of this isotope in cosmic radiation processes and possible applications of this assay to hydrology and meteorology. The appearance of artificial tritium from thermonuclear explosions made those applications even more obvious.

There was considerable difficulty in counting tritium, owing to its low natural abundance in water, which was of the order $T/H=10^{-18}$ and the low energy of its beta radiation ($E_{\max} = 18.5$ keV). The methods used so far have been based on electrolytic enrichment of water samples and counting of the hydrogen gas activity in GM counters¹⁻⁴. These methods have been widely used to measure tritium concentrations in rain and ground water in order to estimate the 'age' of reservoirs and the holding times of water in the atmosphere and on the lands. The sensitivity of this method was nearly $T/H = 10^{-19}$ when correspondingly high initial enrichment of ca. $3 \cdot 10^4$ was used. In one case, diffusion cloud chamber was used as the detecting apparatus⁵ but the results were not quite consistent with those obtained previously.

This paper describes a different approach to natural tritium counting. It is based on a relatively lower enrichment, performed by fractional distillation of water, and on counting the sample in liquid phase, using the liquid scintillation method.

ENRICHMENT

The theory and application of fractionating columns to isotope separation has been described by DOSTROVSKY *et al.*^{6,7} In Fig. 1, a 40 l. fractionating column used for first stage enrichment, providing tritium enrichment of 27, is shown. The final enrichment q_{∞} is given by the relation:

$$q_{\infty} = \frac{N_{\infty}}{N_0} = \frac{\alpha(R + B + HZ) e^{\omega Z}}{R + \alpha B e^{\omega Z} + \frac{H}{\omega} (e^{\omega Z} - 1)}$$

where: N_0, N_∞ — initial and final tritium concentrations,
 R — reservoir
 B — boiler
 H — liquid hold-up per unit height
 ω — constant dependent on flow rate and
 α — separation factor (single plate)
 Z — height of column

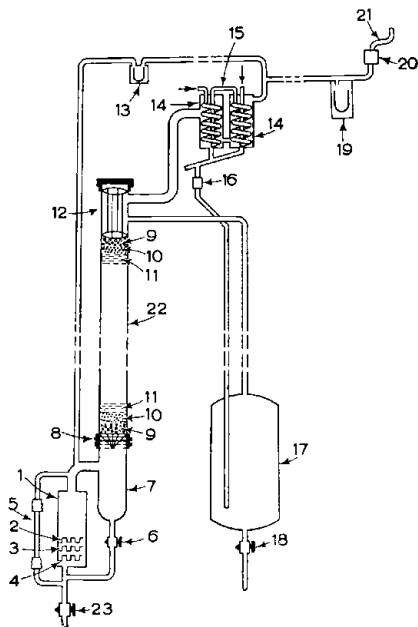


Fig. 1. Fractionating column 40 l.

The results of a calibration run for this column, are shown in Fig. 2. Results for D, T and O¹⁸ are given as function of distillation time. The second stage of enrichment is performed in a smaller column, having 1 l. reservoir, 80 ml boiler and providing tritium enrichment of 10. Operating time of the larger column is 8 weeks, smaller—4 weeks.

SAMPLE PREPARATION

In order to make use of the liquid scintillation method, the enriched water sample is shaken with toluene. In the presence of 50% molar sulfuric acid, the *o*- and *p*-hydrogens of toluene exchange readily with the hydrogen ions while *m*-position hydrogens react about 50 times slower.^{8,9} In order to avoid dilution of the tritium, SO₃ is added gradually to the water sample until the proper concentration is achieved.¹⁰ In the experimental conditions

of this work 25% of the tritium content of the water sample could be transferred into the toluene¹¹ taking into account sulfonation of toluene and separation losses.

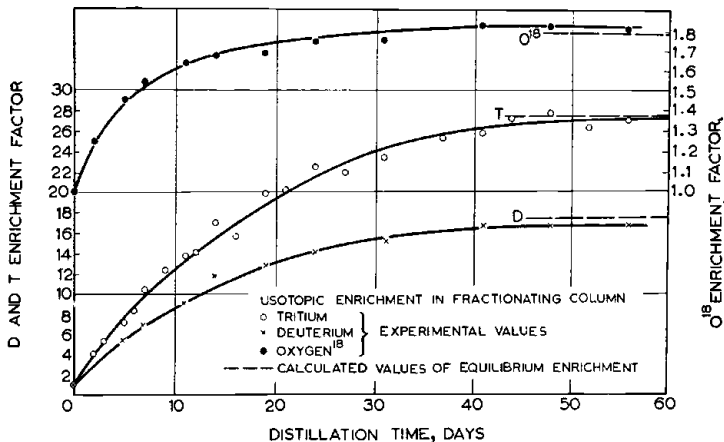


Fig. 2. Isotopic enrichment of D, T and O¹⁸ as function of distillation time.

Figure 3 shows the amount of tritium exchanged as function of time, and the amount of sulfonation of toluene. The toluene is used as scintillator solvent with 3 g/l. PPO and 0.1 g/l. POPOP. The counting container is a 2 in. diameter glass tube with glass plate windows, flame sealed at both sides. Its volume is 75 ml, including a reserve volume on top to allow for contraction on cooling. The solution is flushed with argon and flame sealed. The sides are chemically silvered on the outside.

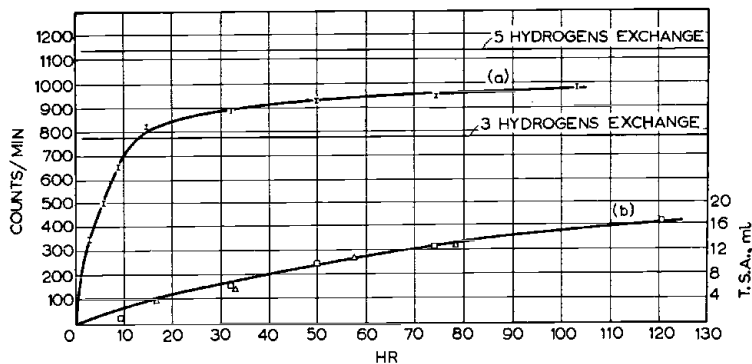


Fig. 3. Tritium exchange between sulfuric acid (48.5% molar) and toluene.

COUNTING APPARATUS AND PROCEDURE

Counting is performed in coincidence, using two selected 2 in photo-multipliers. The tubes and scintillator assembly are cooled to -70°C in order

to decrease the dark current and increase scintillation efficiency. High pulses are fed into an anticoincidence circuit, and do not contribute to the background. (Fig. 4). Light-dark current has been proved to be negligible.

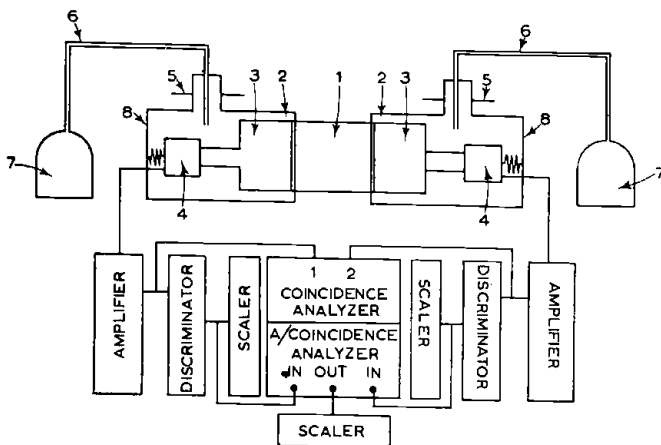


Fig. 4. The liquid scintillation counting assembly.

1. Liquid scintillator cell
2. Photomultipliers
3. Regulated liquid air supply.

Total efficiency for tritium is 45% in these conditions, while the optimum sample to background conditions are obtained at 25% efficiency. The remaining background in these conditions is 120 counts/min with $\sigma = 2$ counts/min. The limiting sensitivity, considering the enrichment and exchange efficiency is $T/H = 10^{-18}$.

EVALUATION OF THE METHOD

It seems, that at present the scintillation method is more complicated, and one order of magnitude less sensitive than the gas counting method. On the other hand, the fractionating method of enrichment seems to be more accurate than the electrolytic method. In addition while the gas phase method is now hard to improve upon, the scintillation counting method may be expected to improve significantly with advances in scintillator efficiency, photosensitivity, supply of non contaminated components in the counting apparatus, and development of high speed coincidence circuits.

APPLICATIONS

Examples of applications are:

- (1) Measurement of rain activity in April 1954, following the large thermonuclear explosions. The activity found was that measured in the U.S. at that period, indicating an upper limit for transit-time of tropospheric moisture.

(2) Measurement of ground water activity in a newly drilled well located at the Arava Valley, connecting the Dead Sea with the Red Sea. The activity found was consistent with the hypothesis of yearly replenishment of the ground water reservoir, and with the amount and activity of rains following the explosions.

(3) Measurement of Dead Sea activity at 100 m depth. This has been found to be higher than could be explained from the known water balance and rain activities in this area, or by any other known tritium production process.

All these results should be considered tentative until more data and experience in operation of this method give indications of consistency of results and freedom from contamination in sample preparation.

REFERENCES

- ¹ S. KANFMAN and W. F. LIBBY. *Phys. Rev.* **93**, 1337 (1954).
- ² H. BUTLER and W. F. LIBBY. *J. Inorg. Nucl. Chem.* **1**, 75 (1955).
- ³ F. BERGMANN. Nuclear processes in geological setting. *Nat. Acad. Sci. Nat. Res. Council. Publication* **400** (1956).
- ⁴ R. M. BROWN and W. E. GRUMMIT. *Canad. J. Chem.* **34**, 220 (1956).
- ⁵ E. L. FIREMAN and D. SCHWARZER. *Phys. Rev.* **94**, 385 (1954).
- ⁶ I. DOSTROVSKY, J. GILLIS, D. R. LLEWELLYN and B. H. VROMEN. *J. Chem. Soc.* 3517 (1953).
- ⁷ I. DOSTROVSKY, J. GILLIS and D. R. LLEWELLYN. *L. Farkas Memorial Vol., Res. Council. Israel Spec. Publ. No. 1.* (1952).
- ⁸ S. OLSSON and L. MELANDER. *Acta Chem. Scand.* **8**, 523 (1956).
- ⁹ V. GOLD and O. P. N. SATCHELL. *J. Chem. Soc.* 2743 (1956).
- ¹⁰ P. AVINUR. In press.
- ¹¹ P. AVINUR and A. NIR. *Bull. Res. Council. Israel.* In press.