Tritium in Nature[1]

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IN RECENT YEARS the existence of natural radiocarbon produced by the action of neutrons from cosmic radiation on nitrogen in the atmosphere has been demonstrated (*1*). The possibility that the helium-3 isotope found in atmospheric helium has its origin in the production of tritium by the action of the cosmic radiation on the air (*2*) has led us to examine surface waters for tritium.

The authors are indebted to the Norsk Hydro-Elektrisk Kvoelstofaktievelskab of Oslo, Norway, for its whole-hearted cooperation in this research, and particularly to Directors E. Uri and V. Stephansen and Engineers J. Brun and F. Bugge. The State Department, especially Henry S. Villard and Lt. Col. Lahlum, of the U. S. Embassy in Oslo, were most helpful in arranging the transportation of samples to Temple University. In addition, we wish to thank Harold C. Urey, H. S. Taylor, A. Farkas, M. L. Oliphant, Sir John Cockcroft, Sir James Chadwick, N. Feather, and Harry Thode for their assistance in the procuring of the samples. We are further indebted to the Houdry Process Corporation, of Philadelphia, for a number of mass analyses. The assistance of A. D. Kirshenbaum and Edward Nodiff is also gratefully acknowledged.

The procedure has been to measure highly concentrated heavy water samples that have been produced from surface waters and should contain any natural tritium at about one millionfold higher concentration than the original water. It has been observed that such samples are indeed radioactive to an extent corresponding to a natural abundance of tritium of about one atom in 10^{18} atoms protium. All the measurements completed to date have been made on Norwegian waters, although measurements on waters from other localities are in progress.

The first sample examined was that described by Rutherford (*3*), which was 11 ml of heavy water made from 13,000 tons of ordinary Norwegian surface water in 1935–36. It was in this sample that F. W. Aston tried to detect the presence of tritium with his mass spectrograph and concluded that T/D must be less than 2 in 10^5. Our measurements gave a tritium mole fraction of 3.2×10^{-12}. Using the probable enrichment factor for the electrolytic concentration process of 9×10^6, we have arrived at a natural abundance of 1×10^{-18} moles of tritium per mole of ordinary hydrogen in Norwegian surface water. A second sample furnished by M. L. Oliphant from the same source but less highly enriched (calculated enrichment factor of 6×10^5) gave 5.3×10^{-13} for the mole fraction of tritium, corresponding again to a natural abundance of 1×10^{-18}. The possibility existed that these samples had been contaminated with artificial tritium in Rutherford's laboratory, so we requested the manufacturers of these original samples, the Norsk Hydro-Elektrisk Kvoelstofakievelskab, of Oslo, to prepare another set of samples analogous to those prepared for Lord Rutherford. Through the kindness of E. Uri and J. V. Stephansen three samples were prepared by J. Brun and F. Bugge at the Vemork plant, by the electrolytic method: Sample A, 2 ml of water taken from the electrolyte after the reduction of 2,950 ml of 99.74 per cent ordinary D_2O to a volume of 15 ml; Sample B, 5 ml of water formed by the combustion of electrolytic gases during the electrolysis between 20 and 15 ml electrolyte volume; Sample C, 2 ml of residue from the electrolysis after reduction of 13 ml of Sample A to 3 ml volume. The original D_2O used in the final concentration steps was also measured.

The original *ordinary* water for these samples, according to Norsk Hydro, "came from Lake Mösvann, which collects the water from the mountain plateau Hardangervidda in southern Norway. The height above sea level is everywhere higher than 900 meters. The Lake Mösvann water was taken into the plant at the end of January 1948, and it is likely that it originated from snow fallen during the winter 1946–47."

All D_2O samples were redistilled, combined at room temperature with pure, freshly dehydrated CaO to $Ca(OD)_2$, and the latter completely converted with zinc dust, at red heat, into deuterium gas, in line with the equation

$$Ca(OD)_2 + Zn \rightarrow Ca\,Zn\,O_2 + D_2 \uparrow .$$

In this reaction isotopic fractionation is practically excluded because of high temperature and complete conversion. All samples were analyzed on a standard Consolidated Engineering Corporation mass spectrometer for both chemical and isotopic composition. All samples were "monitored" to pure deuterium content. Our results to date are given in Table 1.

Taking the probable enrichment factor for Sample

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TABLE 1

DATA FOR TRITIUM IN NORWEGIAN WATERS

Sample	Probable enrichment	Observed tritium content, g-At.T/g.At.D.	Calculated natural abundance, g-At.T/g.At.H^1	Age* of sample	Corrected natural abundance, g-At.T/g.At.H^1
Rutherford	9×10^6	3.2×10^{-12}	0.4×10^{-18}	1935→1949; 14 y	0.9×10^{-18}
Oliphant	1.4×10^6	5.3×10^{-13}	0.4×10^{-18}	1935→1949; 14 y	0.9×10^{-18}
Sample A	1.5×10^6	$1.6 \times 10^{-12} \pm 5\%$	1×10^{-18}	Jan. 1948→1950; 1.5 y	1×10^{-18}
Sample C	2.8×10^6	$2.8 \times 10^{-12} \pm 5\%$	1×10^{-18}	Jan. 1948→1950; 1.5 y	1×10^{-18}
Original D_2O	6×10^4	$0.049 \times 10^{-12} \pm 10\%$	0.8×10^{-18}	Jan. 1948→1950; 1.5 y	0.8×10^{-18}

* The years given are those for the collection of water sample and counting. The *actual* age, based on the original snowfall or rainfall, is greater but is not known to us with any accuracy.

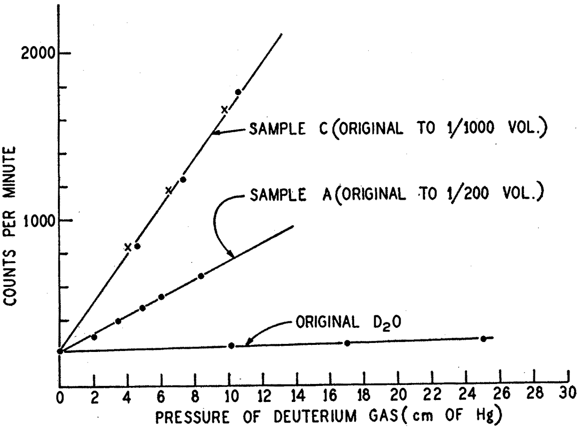
A as 1.5×10^6, we calculate the natural abundance to be 1.3×10^{-18} moles of tritium per mole of ordinary hydrogen in surface water. The results on Sample C and the original D_2O are in fair agreement with this.

The separation factors assumed in the calculation of probable enrichment were 6 for deuterium vs. protium, 15 for tritium vs. protium (*4*), and 2.5 for deuterium vs. tritium. The rather considerable uncertainties in these separation factors as applied to the actual process utilized make it probable that our figure of 10^{-18} for the absolute abundance of natural tritium in Norwegian surface waters is not accurate to a factor better than 10.

The fact that the activity is due to tritium is insured by the following chemical considerations:

1. The activity was concentrated as a water molecule by a factor of up to 10^7-fold; in the case of the last 3 samples of Table 1, it was followed from a 60,000-fold concentration up to 2.8×10^6-fold enrichment.
2. Each sample was distilled from concentrated potassium hydroxide solutions during the three to four concentration stages. The final samples of D_2-gas were purified and dried over soda lime to exclude any trace of atmospheric cosmic CO_2 in the storage bulb itself.
3. The experimental separation factor of our activity to deuterium = 2.8, in going from the original D_2O to Sample A, and = 2.5 in case of original D_2O to Sample C, in good agreement with the theoretical value of 2.5 (Table 1.)

Measurement of the tritium content of the deuterium samples was made by filling an ordinary flat-ended, brass wall Geiger counter with a mixture of deuterium (or hydrogen for the background determination), argon, and ethylene. The pressures used were 1–30 cm of the hydrogen gases, 3–6 cm of argon, and 1–2 cm of ethylene. It was observed that this mixture had excellent counting characteristics, very high efficiency as judged by response to an external source in comparison with a standard argon-ethylene filling in the same counter, and very satisfactory plateaus. The difference between the count rate with the deuterium filling and with an ordinary hydrogen filling was plotted as a function of pressure of deuterium. This gave straight lines, the slopes of which were taken as measures of the inherent specific activities of the deuterium samples. Fig. 1 presents these data for the recent Norwegian samples. A correction of about 3.5 per cent for end loss was made (*5*). The counter dimensions were 2″ × 17″. The half-life of tritium was taken as 12.4 years.



COUNTS vs PRESSURE DATA FOR NORWEGIAN DEUTERIUM SAMPLES

FIG. 1.

These results, although of limited accuracy and applicable to only one locality, make it seem rather probable that a considerable fraction, if not all, of the helium-3 observed in atmospheric helium does indeed have its origin in the cosmic ray-produced tritium. Further studies should afford a more exact check on this point.

It is worth while to point out that with a concentration of 3.10^{-18} g/g protium, cosmic tritium is by far the rarest atomic species discovered in nature. It thus has no military significance.

References

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