Standardization of natural tritium measurements[1]

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ABSTRACT

A series of water samples prepared in Stockholm from tritium-free water and NBS-standard tritiated water have been used to check the accuracy of natural tritium measurements in our three laboratories. There is evidence of pick-up during analysis to the extent of 1–2 TU in one of the laboratories, but otherwise all results from the three laboratories agreed well with the values calculated from preparation of the samples. Agreement was also obtained on a second series of reference samples prepared and distributed by the International Atomic Energy Agency, Vienna.

1. Introduction

Measurements of tritium in natural water, hydrogen, and methane are now being made at a number of laboratories. The procedures used for both the isotopic enrichment and the low level counting are complicated and vary between laboratories.

Geophysical interpretation of the data involving correlation of results from several laboratories is often made by scientists not familiar with the analytical techniques. Some discrepancies have occurred between measurements at different laboratories on similar water samples, as shown by ÖSTLUND and LUNDGREN (1964). It has become increasingly important therefore to make comparisons between laboratories. For this purpose a number of large water samples of known tritium content was prepared in Stockholm and Vienna from dead water and NBS-standard tritium water. Portions of these samples were sent to various other laboratories and results of the analysis of these solutions in Stockholm, Chalk River and La Jolla are presented in this paper.

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[3] Recent redetermination by the NBS of the spec. activity of this water by gas counting techniques, indicates that the 1954 standardization may have been too high by 2.0 ± 1.0 % only. (Circulate letter from W. B. MANN, Chief Radioactivity Section, NBS).

In the following discussion it should be remembered that hydrogen is said to have a tritium assay of 1 TU when the tritium molar fraction of hydrogen, T/H, is 10^{-18}. Water of 1000 TU has a tritium disintegration rate of 7.18 dis min^{-1} ml^{-1} based on a half-life of 12.26 years (JONES, 1955).

2. Preparation of Stockholm reference samples

Water samples of known tritium content were prepared in Stockholm from tritium-free water and NBS-standard tritiated water.

PRIMARY STANDARD SOLUTION:

Tritiated water from the National Bureau of Standards, Washington, D.C., U.S.A. stated to give $1.33 \times 10^4 (\pm 1.5\ \%)$ dis sec^{-1} ml^{-1} on 20 August 1954, i.e. 7.34×10^7 TU on 1 January 1962, using 12.26 years for the half-life of tritium.[3]

TRITIUM-FREE WATER

Bastkärn mine water (cf. below, Table 1, for analysis).

DILUTIONS

All values for Stockholm reference samples refer to 1 January 1962.

(*a*) NBS-1: 3.15×10^5 TU: 1.073 g of NBS standard solution diluted to 250.0 ml with tritium-free water.

(*b*) Stockholm 2000 TU: 31.75 ml NBS-1 diluted to 5000 ml with tritium-free water.

(*c*) Stockholm 100 TU: 15.88 ml NBS-1 diluted to 50.00 kg with tritium-free water.

(*d*) Stockholm 10 TU: 1.52 ml NBS-1 diluted to 48.00 kg with tritium-free water.

(*e*) Stockholm 0 TU: Bastkärn mine water.

(*f*) NES3:2A: 5.08×10^4 TU: A dilution of standard tritiated water supplied by New England Nuclear Corporation, U.S.A. This solution has been found to check with dilutions of the NBS standard (ÖSTLUND, 1962) at 364.2 dis $min^{-1} ml^{-1}$.

Deuterium analyses of all these solutions except NES3: 2A, in the absolute scale of E. ROTH (personal communication, 1963) in which Standard Mean Ocean Water, SMOW, is 161.9 ± 0.5 pp,m (c.f. Craig 1961).

3. IAEA samples

These samples were prepared by the International Atomic Energy Agency laboratories, Vienna. NBS Standard 4926[1] was diluted with tritium-free water (analyzed by the Stockholm Laboratory) from the Sabi River Valley, Southern Rhodesia.

4. Analysis

The isotopic enrichment and counting procedures used in the three laboratories are rather different (ÖSTLUND, 1962; ÖSTLUND and WERNER, 1962; BROWN and GRUMMITT, 1956; BAINBRIDGE, 1963). The Chalk River Laboratory concentrates by batch electrolysis to about 70 mg of water, then counts the sample as hydrogen in a 70 ml Geiger counter. The Stockholm Laboratory electrolyzes samples to 1 g of water by periodic additions and counts them as hydrogen in a 1 litre Geiger counter. The La Jolla system enriches samples in batches to about 4 g of water and counts them as ethane in a high pressure proportional counter. In Stockholm and Chalk River the recovery of tritium in the enrichment process is estimated from the measured recovery of deuterium. In Stockholm this is achieved by mass-spectrometric, in Chalk River by infrared analysis (STEVENS and THURSTON, 1954). The tritium enrichment factors were calculated with the formulae and constants determined by ÖSTLUND and WERNER (loc. cit.) In La Jolla the enrichment factor, β, for tritium was constant enough to allow the omission of deuterium measurements.

TABLE 1. *Stockholm measurements on Stockholm reference samples.*

Sample	Run No.	Enrichment V_0/V	Measured tritium assay, TU
Stockholm 0 TU (Bastkärn mine water)	StT-458	80	0.16 ± 0.24
	460	90	0.3 ± 0.3
	696	90	0.14 ± 0.25
	697	90	0.12 ± 0.25
Stockholm 10 TU	StT-457	80	10.1 ± 0.5
	487 I	60	10.0 ± 0.4
	487 II	70	10.5 ± 0.4
Stockholm 100 TU	StT-459	80	105 ± 3
	488 I	40	104 ± 3
	488 II	70	105 ± 3
	488 III	70	102 ± 3
Stockholm 2000 TU		Direct	2085 ± 25
		Direct	2010 ± 25
		Direct	2010 ± 30
NES3 : 2A 50,800 TU		Direct	Secondary standard

The presented results include the estimated overall standard error (1 σ) for the enrichment and counting. "Direct" in the "enrichment" column indicates that sample was counted without enrichment.

TABLE 2. *Chalk River measurements on Stockholm reference samples.*

Sample	Run No.	Enrichment V_0/V	Measured tritium assay, TU
Stockholm 0 TU	X-20	1,880	1.78 ± 0.12
	X-20 R	15,150	0.76 ± 0.04
	X-20 R2	2,440	1.15 ± 0.09
Stockholm 10 TU	X-21 R	3,140	11.2 ± 0.3
	X-21 R2	2,210	13.1 ± 0.4
Stockholm 100 TU	X-22	1,860	96.0 ± 2.5
	X-22 R	2,390	102.0 ± 2.6
Stockholm 2000 TU	X-23	156	$2,040 \pm 50$
	X-23 R	140	$2,070 \pm 52$
	X-23 d	Direct	$2,010 \pm 300$[a]
NES3 : 2A	(1)	Direct	$50,800 \pm 310$
	(2)	Direct	$51,700 \pm 310$

[a] Large uncertainty on direct counting at this low concentration because of the small volume of the Chalk River counter.

[1] See note 3, preceding page.

TABLE 3. *La Jolla measurements on Stockholm reference samples.*

Sample	Run No.	Enrichment V_0/V	Measured tritium assay, TU
Stockholm 0 TU	382	125	<0.08[a]
Stockholm 10 TU	379	125	10.02 ± 0.2
Stockholm 100 TU	375	Direct	101 ± 1
	384	20	108 ± 4
	406	23	104 ± 4
Stockholm 2000 TU	368	Direct	2024 ± 30
	376	Direct	2002 ± 20

[a] 95% confidence.

5. Discussion

The results reported in the accompanying tables indicate satisfactory agreement between analyses in the three laboratories at concentrations greater than 10 TU. Samples measured by direct counting demonstrate the equivalence of the different counting systems. The agreement of results for the 2000 and 100 TU samples shows that no discrepancy is introduced by the enrichment process and methods of estimating tritium recovery. There is good correspondence between results obtained in one laboratory by direct counting and in another by enrichment and counting in a smaller volume.

At the 10 and 0 TU levels, the Stockholm and La Jolla Laboratories obtain satisfactory results, but it is apparent that contamination of 1–2 TU occurs in the course of analysis at Chalk River. A "background" level of this magnitude has been suspected at Chalk River in the past since no samples analyzed there have shown a concentration of less than 0.5 TU. This

TABLE 4. *Stockholm Measurements on IAEA standards referred to 14 October 1962.*

Sample	Run No.	Enrichment V_0/V	Measured tritium assay, TU
IAEA 112 TU	StT-563	80	115 ± 3
	574	70	114 ± 3
	598	50	112 ± 3
IAEA 1448 TU	StT-690	Direct	1410 ± 30
IAEA 1.042×10^5 TU	StT-691	Diluted	$(1.041 \pm 0.010) \times 10^5$

TABLE 5. *Chalk River measuremens on IAEA standards referred to 14 October 1962.*

Sample	Run No.	Enrichment V_0/V	Measured tritium assay, TU
IAEA 112 TU	X-29	1425	113.5 ± 2.3
IAEA 1448 TU	X-31	116	1432 ± 28
IAEA 1.042×10^5 TU	X-30	Direct	$(1.050 \pm 0.006) \times 10^5$

may be due to the dispersal of tritium from several large deuterium moderated reactors about 15 km from the laboratory. The usual Chalk River analysis for very low assays involves three or four stages of electrolysis with distillations between stages. All transfers are by vacuum distillation and the electrolytic gases are discharged from the cells through drying tubes. However, the cells are open during assembly and the multiple manipulations inevitably provide opportunity for exchange with atmospheric moisture. It is significant that a lower value (X–20 R) was obtained when a larger sample was put through the same number of cells and transfers (three) by a system of continuous feed of sample to the first stage.

The Stockholm Laboratory has analyzed a number of Ottawa precipitation samples dating from 1952–56 which have been stored in glass bottles at Chalk River since their collection and original analysis in the Chalk River Laboratory. Of 16 samples, 8 checked within 15 % of the original Chalk River analyses, 15 checked within

TABLE 6. *Summary of measurements of reference samples.*

Sample/Laboratory	Stockholm	Chalk River	La Jolla
Stockholm 0 TU	0.17	0.90	<0.08
Stockholm 10 TU	10.2	11.9	10.0
Stockholm 100 TU	104	99	102
Stockholm 2000 TU	2035	2055	2009
St 50,800 TU	Sec. stand.	51,250	–
IAEA 112 TU	114	113.5	–
IAEA 1448 TU	1410	1432	–
IAEA 1.042×10^5 TU	1.041×10^5	1.050×10^5	–

30 % and one sample of doubtful original analysis, analyzed at double the original value. All except two of the Stockholm values were higher than the original Chalk River analyses, suggesting some contamination by tritium during storage.

6. Conclusion

The three laboratories in Stockholm, Chalk River and La Jolla measure tritium at concentrations occurring in natural waters with an accuracy of $\pm 4\%$, based on the 1954 NBS tritium standard. However, there is evidence of contamination during analysis to the extent of 1–2 TU in the Chalk River Laboratory. The overall obtainable accuracy is better than necessary for most geophysical applications of tritium data. It is also obvious that the IAEA and the Stockholm reference samples are completely interchangeable.

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