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INTERLABORATORY COMPARISON OF ANALYSIS OF TRITIUM
IN NATURAL WATERS

T. Florkowski, B.R. Payne, G. Sauzay

International Atomic Energy Agency, Vienna

Abstract

The results of analyses of Tritium in natural waters made by 35 laboratories are compared. Three water samples in a concentration range of 10 - 250 T.U. were used for the intercomparison. Analyses were effected by liquid scintillation and gas counting with and without electrolytic enrichment. The results form the basis for conclusions regarding the optimal concentration range for each method of assay.

Interlaboratory Comparison of Analysis of Tritium
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1. INTRODUCTION

The International Atomic Energy Agency recently compared results of analyses of tritium in natural water. The aim was to enable the increasing number of laboratories in various countries to compare their results with others and to evaluate possible systematic errors due to calibration of the instruments or the procedure used.

Three water samples (prepared by spiking tritium-free water) in a tritium concentration range of 10 - 250 T.U., were distributed to 38 laboratories. Results from 35 laboratories were received with indications of what technique had been used for the tritium assay.

2. RESULTS

The results of the measurements are presented in Table I in three main columns, corresponding to the three samples T1, T2 and T3. In each column a subdivision is made for different measurement procedures. Some of the laboratories which use various procedures presented results for each one.

3. EVALUATION OF RESULTS

The aim of the evaluation was the determination of mean values of T1, T2 and T3 for each measurement method, the spread between results represented by a standard deviation and possible systematic differences between various methods of assay. The evaluation should conclude in an optimal method for tritium assay in various concentration ranges.

As the true values of T1, T2 and T3 are not known, the mean values are taken as the best estimate of the "true values". In order to determine the best mean value, the following procedure was adopted:

3.1. In the first approach the arithmetical means were calculated, i.e. the same weight was given to each measurement, independent of analytical errors.

$$M_1 = \frac{1}{n} \sum_1^n m_i$$

The standard deviation of a single measurement is given by

$$\sigma_1 = \sqrt{\frac{1}{n-1} \sum_1^n (m_i - M_1)^2}$$

The results are given in Table II. Measurements, most likely incorrect, (marked with an asterisk in Table I) were not included in this computation.

3.2. In the second approach individual results were weighted by the inverse of the square of the analytical errors claimed by the laboratories. For the first calculations of the mean all data were included. The mean and its standard deviation were calculated using the formulae:

$$M_2 = \frac{\sum_1^n \frac{m_i}{\sigma_i^2}}{\sum_1^n \frac{1}{\sigma_i^2}}$$

and

$$\sigma_2 = \frac{1}{\sqrt{\sum_1^n \frac{1}{\sigma_i^2}}}$$

Results are also given in Table II.

The data from each laboratory were then compared with the estimated means using the following formula:

$$k = \frac{m_i - M_2}{\sigma_i}$$

If k was higher than 3 (i.e. the individual results differ from the mean value by more than 3σ assigned to this result) the data were assumed to be unacceptable, probably due to contamination or to some other causes during the assay. This is illustrated in Table III.

In the next computation the mean value M_2 was calculated again using the same method but excluding those having a value of k higher than 3 (Tables III and IV). Tables III and IV provide a basis for a detailed analysis of possible systematic errors of individual laboratories. If for a given laboratory k always has the same sign, positive or negative, a systematic error (e.g. due to incorrect calibration) could be suspected.

3.3. In order to compare different methods of measurements, the ratios of mean values (and their standard deviation) were computed as follows:

	DG	EG/DG	ES/DG
T1	1	1.027 (0.098)	1.125 (0.136)
T2	1	1.023 (0.025)	1.156 (0.044)
T3	1	0.999 (0.014)	1.034 (0.015)

A systematic shift of the ES method compared with gas counting methods can be suspected.

Different methods can be further compared by the percentage error of a single measurement. For the computation the same standard deviation of a single measurement belonging to the same population was assumed, i.e.

$$\sigma_i = \frac{\sigma_2}{M_2} \sqrt{n}$$

where n is the number of measurements used to calculate M_2 and σ_2

	DG	EG	ES	DS
T1	25%	5.4%	20%	
T2	6.4%	4.4%	9.4%	
T3	2.6%	3.5%	3.8%	9.6%

These figures plotted on a graph (Fig.1) relating tritium concentration and percentage error provide interesting information on the optimal concentration range for each method of assay. The conclusion is as follows:

a) Enrichment and gas counting is most accurate in the concentration range from 0 to 80 T.U. For a higher concentration, direct gas counting is more accurate since the error of the enrichment process is the overall determining factor in the final estimate of σ .

b) Scintillation counting of enriched samples becomes equivalent to gas counting of enriched samples for concentrations higher than about 300 T.U.

The above treatment should only be considered as a rough measure of analytical performance since only three samples have been used in the intercomparison. Also many parameters like enrichment factor, counting time, etc. were rather variable in the various laboratories.

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The authors wish to express their appreciation of the cooperation of all laboratories who have contributed to this intercomparison.

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TABLE I

Results of Tritium Intercomparison

Laboratory	T1			T2			T3			
	DG	EG	ES	DG	EG	ES	DG	EG	DS	ES
1	8.4±2.8	9.6±0.5	12.3±2.2	42.3±3.5	42.2±1.6	45.7±3.5	234±6	246±5	265±45	251±11
2			4.4±0.9*			31.5±1.5*			220±19	
3		8.5±0.9			35.4±3.6*			199±20*		
4	13.2±4.0	9.9±0.7	14.0±7.0	43.5±4	48.0±3	47.5±1.0	241±5			255±18
5		10.8±0.5			40.9±2.0			217±11		
6		8.5±1.2			33.2*			222±11		
7			15±12*B.S.			46±12 B.S.				258±15 B.S.
8			8.3±1.5			45.0±6				247±20
9			12.0±2.0			49.0±3				244±8
10			8.9±1.7			43.0±6				249±25
11			14.0±3.0			50.0±3				249±4
12			21.0±2.5*			52.0±6				245±17
13						56.4*B.S.				310*B.S.
14	9.0±1.1			40.7±1.4			243±5			
15		8.1±0.3			38.2±1.5*		249±7			
16		9.5±0.3			43.3±1.0			238±7		
17				37.0±7*			250±10			
18	9.0±4.0			41.0±4			265±5			
19		10.4±2.0			55.6±5*			275±17*		
20										296±90*
21		14.8±0.9*			41.5±2.5			271±16*		
22						52.0±6.3				268±66
23			19.1±7.6*			46.8±7.6				252±9
24	7.4±4.4			47.0±7.0			262±8			
25	11.5±3.0			44.6±3.5			256±9			
26			13.2±2.8			107.4±9*				302±13*
27		10.2±1.0			47.6±1.5			279±5		
28	9.9±4.8			44.4±6.6			240±24			
29		11.6±0.7			47.0±3.0		227±12			
30		22 ± 2*			50±3			200±10*		
31		9.3±0.5			43.3±2.0		249±19			
32									250±24	
33		8.9±0.4			42.0±1.6			241±6		
34			40*D.S.			60*D.S.			280*	
35		9.3±0.4		42.0±1.6	42.8±1.4		235±3		242±19	

DG Direct Gas Counting

EG Enrichment and Gas Counting

DS Direct Liquid Scintillation Counting

ES Enrichment and Scintillation Counting

BS Benzene Synthesis and Liquid Scintillation Counting

1 International Atomic Energy Agency Vienna, Austria

2 Atomic Energy Commission Sutherland, Australia

3 Commonwealth Scientific and Industrial Research Organiz. Adelaide, Australia

4 Bundesversuchs- und Forschungsanstalt Arsenal Vienna, Austria

5 Atomic Energy of Canada Ltd. Chalk River, Canada

6 Saskatchewan Research Council Saskatoon, Canada

7 Danish Isotope Centre Copenhagen, Denmark

8 Bureau de Recherches Géologiques et Minières Orleans, France

9 Centre d'Etudes Nucléaires Grenoble, France

10 Centres de Recherches Géodynamiques Thonon-les-Bains, France

11 Université de Bordeaux Talence, France

12 Gesellschaft für Strahlenforschung m.b.H. München, Germany

13 Institut für Bodenkunde Bonn, Germany

14 Niedersächs. Landesamt für Bodenforschung Hannover, Germany

15 Universität Heidelberg Heidelberg, Germany

16 University of Iceland Reykjavik, Iceland

17 Tata Institute of Fundamental Research Bombay, India

18 The Weizmann Institute of Science Rehovot, Israel

19 The Institute of Physical and Chemical Research Tokyo, Japan

20 Ministry of Works Nairobi, Kenya

21 The Institute of Nuclear Sciences Lower Hutt, New Zealand

22 Hydrological Enterprise Warsaw, Poland

23 University of Stockholm Stockholm, Sweden

24 Universität Bern Bern, Switzerland

25 University of the Witwatersrand Johannesburg, South Africa

26 ME Regional Radioisotope Centre Cairo, U.A.R.

27 UK Atomic Energy Authority Wantage, U.K.

28 Isotopes Inc. Palo Alto, U.S.A.

29 Isotopes Inc. Westwood, U.S.A.

30 New Mexico Institute of Mining and Technology Socorro, U.S.A.

31 University of California La Jolla, U.S.A.

32 University of Hawaii Honolulu, U.S.A.

33 University of Miami Miami, U.S.A.

34 U.S. Geological Survey Denver, U.S.A.

35 U.S. Geological Survey Washington, U.S.A.

TABLE II

Mean Values of Tritium Data

	T1			T2			T3				
	DG	EG	ES	DG	EG	ES	DG	EG	DS	ES	
M_1	9.77	9.58	11.81	43.19	43.90	47.89	245.9	243.2	251.4	251.1	
σ_1	1.98	0.99	2.33	8.11	3.48	3.12	11.5	27.6	22.8	7.2	
M_2	9.33	9.46	8.57	41.73	43.10	40.76	243.6	247.2	237.4	251.6	
σ_2	0.88	0.13	0.58	0.89	0.48	1.06	1.74	2.46	11.34	2.94	
M_2^1	9.33	9.58	10.5	41.73	42.70	48.25	240.6	240.3	237.4	248.9	
σ_2^1	0.88	0.15	0.80	0.89	0.54	1.51	1.86	2.95	11.34	3.02	

TABLE III

Values k

Laboratory	T1			T2			T3			
	DG	EG	ES	DG	EG	ES	DG	EG	DS	ES
1	-0.33	+0.28	+1.70	+0.16	-0.56	+1.41	-1.6	-0.24	+0.6	-0.05
2			-4.6*			-6.17*			-0.92	
3		-1.07			-2.14			-2.41		
4	+0.97	+0.63	+0.78	+0.25	+1.63	+0.67	-0.52			+0.19
5		+2.68			-1.1			-2.75		
6		-0.8						-2.29		
7										
8			-0.18			+0.71				-0.23
9			+1.71			+2.75				-0.95
10			+0.19			+0.37				-0.10
11			+1.81			+3.08				-0.65
12			+4.97*			+1.87				-0.39
13										
14	-0.3			-0.74			-0.12			
15		-4.53*			-3.27*		+0.77			
16		+0.13			+0.20			-1.3		
17				-0.68			+0.64			
18	-0.08			-0.18			+4.28*			
19		+0.47			+2.5			+1.64		
20										+0.49
21		+5.93*			-0.64			+1.49		
22						+1.78				-0.25
23			+3.90*			+0.80				+0.04
24	-0.44			+0.75			+2.3			
25	+0.72			+0.82			+1.38			
26			+1.65			+7.40*				+3.88*
27		+0.74			+3.0			+6.36*		
28	+0.12			+0.40			-0.15			
29		+3.06			+1.3		-1.38			
30		+6.27*			+2.3			-4.72*		
31		-0.32			+0.1		+0.28			
32									+0.52	
33		-1.4			-0.69			-1.03		
34										
35		-0.40		+0.17	-0.21		-2.87		+0.24	

Remarks : Measurement by benzene synthesis and results quoted without analytical error were not included in the statistical evaluation.

TABLE IV

Values k

Laboratory	T1			T2			T3			
	DG	EG	ES	DG	EG	ES	DG	EG	DS	ES
1	-0.33	+0.04	+0.79	+0.16	+0.31	-0.73	-1.1	+1.14	+0.60	+0.19
2			x			x			-0.92	
3		-1.2			-2.03			-2.06		
4	+0.97	+0.46	+0.49	+0.25	+1.77	-0.07	+0.08			+0.34
5		+2.44			-0.9			-2.12		
6		-0.9						+1.66		
7										
8			-1.51			-0.54				-0.09
9			+0.71			+0.25				-0.61
10			-0.98			-0.87				0
11			+1.14			+0.58				+0.02
12			x			+0.62				-0.23
13										
14	-0.30			-0.74			+0.48			
15		x			x		+1.20			
16		-0.27			-0.06			-0.33		
17				-0.68			+0.94			
18	-0.08			-0.18			x			
19		+0.41			+2.58			+2.48		
20										+0.52
21		x			-0.48			+1.92		
22						+0.60				+0.30
23			x			-0.19				+0.34
24	-0.44			+0.75			+2.67			
25	+0.72			+0.82			+1.71			
26			+0.94			x				x
27		+0.62			+3.26			x		
28	+0.12			+2.38			+1.64			
29		+2.89			+1.43		-1.13			
30		x			+2.43			x		
31		-0.56			+0.30		+0.44			
32									+0.525	
33		-1.7			-0.44			+0.12		
35		-0.7		+0.17	+0.07		-1.87		+0.24	