

Homogeneity Assessment for Grass Samples Used for Organically Bound Tritium Proficiency Test

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Outlines


- Introduction
- Theoretical background
- Sample preparation and measurements used for homogeneity check
- Results and discussions
- Conclusions

Short history of “OBT and its analysis” workshop



- 2012: 1st workshop on OBT and its analysis, Balaruc Les Bains – France
- 2013: 2nd OBT workshop: Research, analysis and inter-comparison results, Southampton – United Kingdom
- 2014: 3rd OBT in Ottawa – Canada
- 2015:4th workshop on OBT and its analysis, Bucharest – Romania
- 2016: 5th workshop on OBT and its analysis, Le Main - France





Standardized methods used for homogeneity check

International Standard Organization, ISO, Statistical method for use in proficiency testing by inter-laboratory comparison, ISO 11538:2015

Comparison between the between sample standard deviation, s_s , and standard deviation for proficiency assessment:

$$s_s \leq 0.3 \sigma_{pt}$$

where:

$$s_s = \max \left(0, \sqrt{s_x^2 - (s_w^2/2)} \right)$$

s_x – standard deviation of the sample average;

s_w – within samples standard deviation

Due to the fact that σ_{pt} is not known in advance and it will be calculated as a robust standard deviation of the results reported by the participants, the homogeneity test was conducted using also, the one way analysis of variance ANOVA test.



Preparation of the dried grass batch



The site for sampling vegetation sample was chosen close to Unit 1 of NPP Cernavoda, where it was marked and where the soil and grass was not disturb at all. The green grass was sampled on 23 -Jun -2016 (half a day).The collection surface was : 200 m². Quantity of sample green grass: 48.384 kg.

Cristina Bucur, "The sample preparation for 4th Organically Bound Tritium inter-laboratory comparison exercise", personal communication at 5th Organically Bound Tritium Workshop – Le Mains, 4-7 September 2016

Preparation of the dried grass batch



Sampling method: manual mowers. The sample grass was sorted from the other spontaneous vegetation and only green grass was selected.

Cristina Bucur, "The sample preparation for 4th Organically Bound Tritium inter-laboratory comparison exercise", personal communication at 5th Organically Bound Tritium Workshop – Le Mains, 4-7 September 2016

Preparation of the dried grass batch



The batch of green grass was dried in the oven at 80°C. It was shredded with a Retsch mill grinding, then it was sieved by 2 mm mesh. The operations were repeated until the whole quantity had the grain below 2 mm. The homogenization was performed for 24 hours with a cement mixer with neoprene cover. 10 subsamples of around 50 g were extracted from the bulk sample using the random stratified method.

Cristina Bucur, "The sample preparation for 4th Organically Bound Tritium inter-laboratory comparison exercise", personal communication at 5th Organically Bound Tritium Workshop – Le Mains, 4-7 September 2016



Hydrogen content measurement



The hydrogen content was measured using an elemental analyzer, Flash 2000 (ThermoScientific). The applied procedure is sample combustion followed by gas chromatography. The temperature of Porapak™ column was 65°C, the temperature of detector was 100°C, and that of quartz reactor 950°C. The sample had a weight between 2 to 5 mg, and the measurement uncertainty was 2.15%.

Tritium concentration determination of combustion water obtained from dried grass



1121 Parr bomb



Lyophilisation system

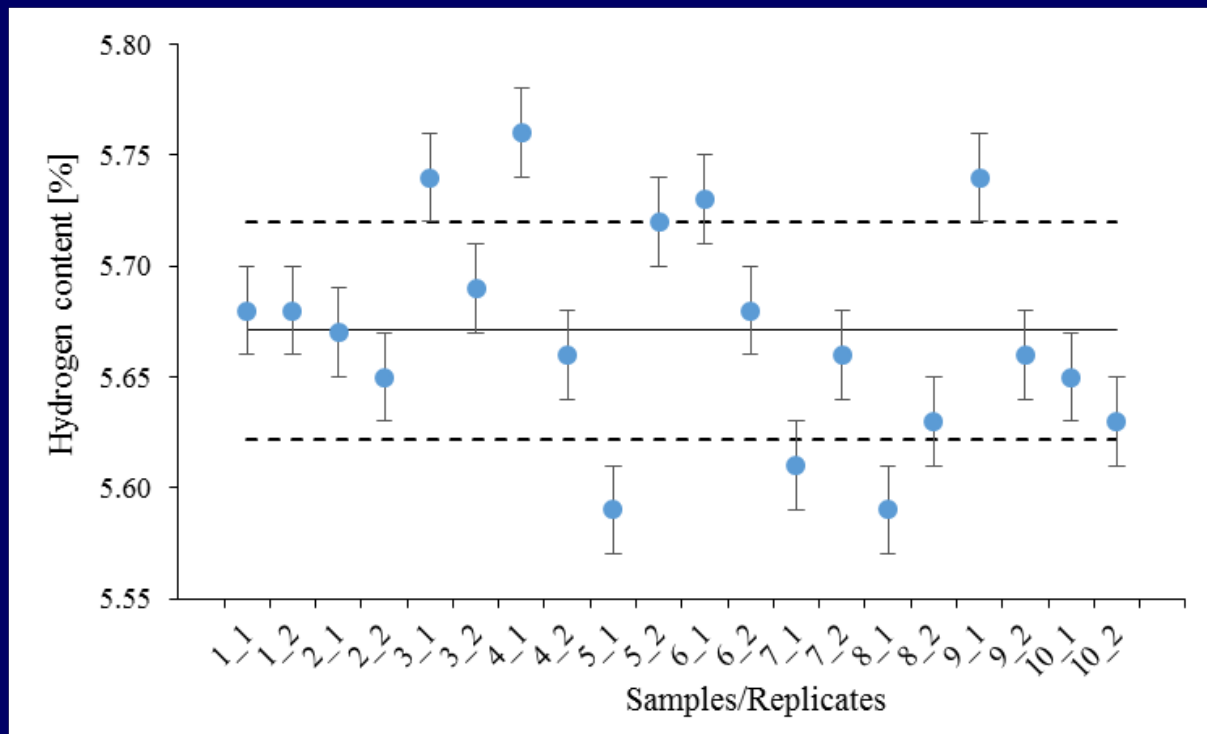


Liquid scintillation spectrometer
Quantulus 1220

The applied procedure, in our laboratory, for total OBT measurements has three important steps: combustion, combustion water purification and liquid scintillation measurement.



Homogeneity check of hydrogen content



Hydrogen content measured in 10 samples of dried grass. Two replicates were performed for each sample. Solid line represents the mean value, and dashed lines represent the standard deviation of the results.

Homogeneity check of hydrogen content



Item	Hydrogen content [%]		x_t	w_t	\bar{x}	s_x	s_w	s_s
	Replicate 1	Replicate 2						
1	5.68	5.68	5.68	0	5.67	0.04	0.05	0.02
2	5.67	5.65	5.66	0.02				
3	5.74	5.69	5.72	0.05				
4	5.76	5.66	5.71	0.10				
5	5.59	5.72	5.66	0.13				
6	5.73	5.68	5.71	0.05				
7	5.61	5.66	5.64	0.05				
8	5.59	5.63	5.61	0.04				
9	5.74	5.66	5.70	0.08				
10	5.65	5.63	5.64	0.02				

Homogeneity check according ISO 11538:2015 for hydrogen content.
 $s_s \leq 0.06$

ANOVA test of hydrogen content

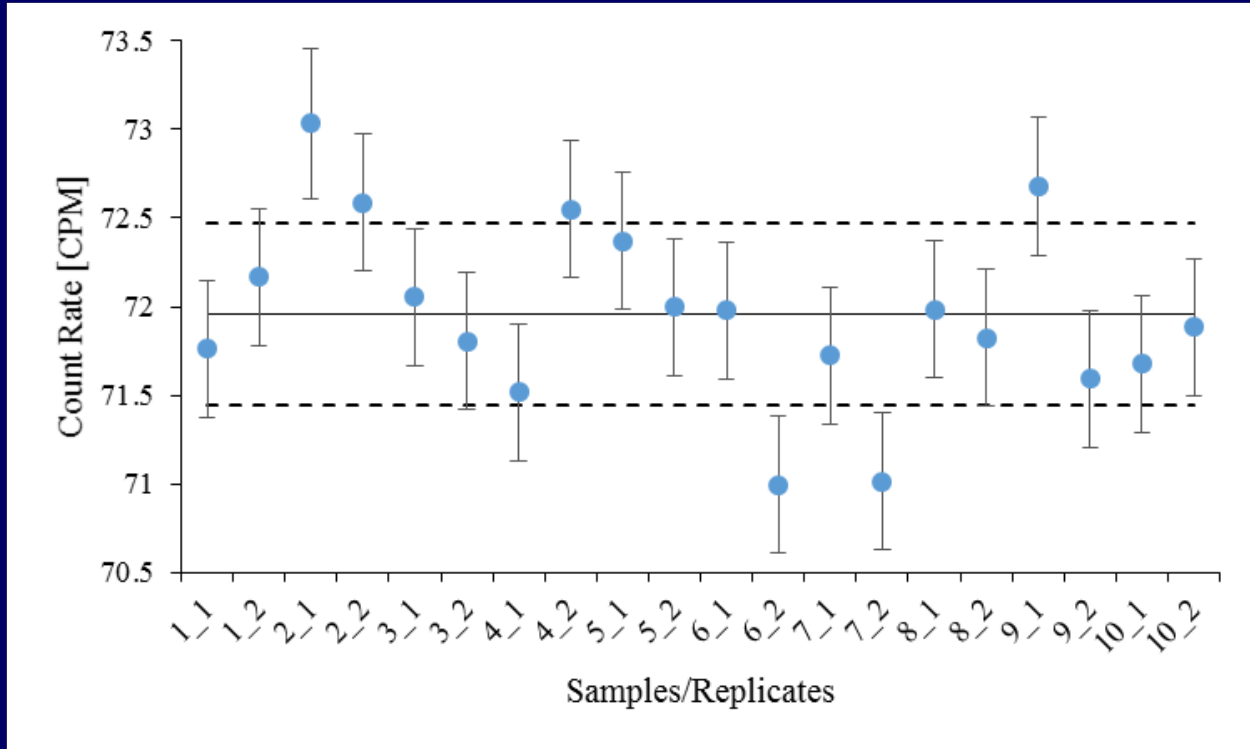


Type of variance	df	SS	MS	F	F _{critical}
Between groups	9	0.024	0.003	1.22	3.02
Within groups	10	0.022	0.002		
Total	19	0.046			

SS-sum of squares, MS-mean squares, df -degrees of freedom, F_{critical} –values for the F distribution at 95% level of confidence.



Homogeneity check for tritium count rate of combustion water



Tritium count rate of combustion water for 10 dried samples of grass and two replicate for each sample. Solid line represents the mean value, and dashed lines represent the standard deviation of the results



Homogeneity check for tritium count rate of combustion water

Item	Tritium Count Rate [CPM]		X_t	W_t	\bar{x}	S_x	S_w	S_s
	Replicate 1	Replicate 2						
1	71.76	72.17	71.96	0.41	71.96	0.41	0.47	0.22
2	73.03	72.59	72.81	0.44				
3	72.05	71.81	71.93	0.25				
4	71.52	72.55	72.03	1.03				
5	72.37	71.99	72.18	0.37				
6	71.98	70.99	71.49	0.98				
7	71.73	71.02	71.37	0.71				
8	71.99	71.82	71.91	0.16				
9	72.68	71.59	72.14	1.09				
10	71.68	71.88	71.78	0.21				

The criteria used for evaluation of the between sample standard deviation was expanded according to ISO11538/2015, paragraph B.2.3., were $\sigma_{\text{allow}}^2 = (0.3\sigma_{\text{theoretical}})^2$, to allow for the actual preparation error and repeatability in the homogeneity check. The theoretical σ associated to the mean counting rate and appropriate parameters from the statistical table for 10 samples of dried grass and two replicate conducted to a critical value of 0.49 higher than s_s .

ANOVA test for tritium count rate of combustion water



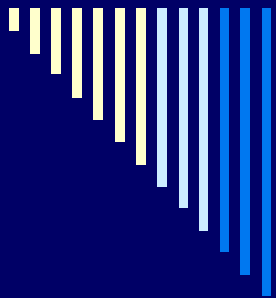
Type of variance	df	SS	MS	F	F _{critical}
Between groups	9	2.83	0.31	1.45	3.02
Within groups	10	2.17	0.22		
Total	19	5			

SS-sum of squares, MS-mean squares, df -degrees of freedom, F_{critical} –values for the F distribution at 95% level of confidence.



Conclusions

- The dried grass batch prepared for the proficiency test of OBT measurement is homogenous for hydrogen content and tritium concentration in combustion water.
- Due to different measurement methods used by the participant laboratories, the homogeneity test is a must for both properties of the material used for proficiency test.
- Further study on the stability of the material is ongoing during the development of the proficiency test.
- This type of material can be a candidate for reference material, but it has an important deficiency, the finite amount that can be prepared, each new batch needing a proficiency test to characterize the material.



Thank you for your attention

