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## ASSESSMENT AND INTERPRETATION OF A ROUND-ROBIN EXERCISE FOR ORGANICALLY BOUND TRITIUM DETERMINATION

N Baglan<sup>1</sup> • E Ansoborlo<sup>2</sup> • C Cossonnet<sup>3</sup> • L Fouhal<sup>4</sup> • E Fourré<sup>5</sup> • A Henry<sup>6</sup> • S B Kim<sup>7</sup> • M Mokili<sup>8</sup> • A Olivier<sup>9</sup> • G Granier<sup>2</sup>

1. CEA/DAM/DIF, F-91297 Arpajon, France. Corresponding author. Email: nicolas.baglan@cea.fr.
2. CEA/DEN/DRCP/CETAMA, BP17171, 30207 Bagnols sur Cèze, France.
3. IRSN/DEI/STEME/LMRE, Bât 501 Bois des Rames, 91400 Orsay, France.
4. CEA/D2S/SPR/LANSE, Bât 310, 13108 Saint Paul lez Durance, France.
5. CEA/DSM/LSCE, Orme des Merisiers Bât 701, 91191 Gif sur Yvette, France.
6. AREVA/NC/DQSSE/PR/E/L, 50444 Beaumont Hague, France.
7. AECL, Chalk River Laboratories, Environmental Technologies Branch, Chalk River, Ontario K0J 1J, Canada.
8. Subatech, Ecole des Mines de Nantes, 4 rue A. Kastler, 44307 Nantes Cédex, France.
9. EAMEA/GEA, BP19-50115 Cherbourg armées, France.

**ABSTRACT.** Tritium occurs in environmental samples in 3 forms: (i) as part of free water (TFWT-tissue-free water tritium), or associated with organic matter in 2 ways, either (ii) bound to oxygen and/or nitrogen atoms of the material as exchangeable organically bound tritium (E-OBT) or (iii) bound to carbon atoms as non-exchangeable OBT (NE-OBT). Analyzing these OBT forms is rather complicated, and several problems have been encountered in developing robust and reproducible analytical procedures, especially for low-level tritium activity. Nevertheless, OBT is nowadays a subject of increasing importance, and the enhancement of determination capabilities is therefore desirable. The CETAMA (Comité d'ETAbblissement des Méthodes d'Analyse) plays an important role in the field of analytical sciences. One of its main tasks is to support French analytical laboratories by providing analytical procedures and organizing user groups and round-robin exercises. The CETAMA recently organized an exercise to determine OBT in an environmental sample. This exercise was conducted to facilitate analytical procedure improvements for the participating laboratories. The results from the exercise demonstrate that several steps of the analytical procedure, such as the combustion and the tritium measurement, are well understood. Moreover, the influences of the drying stage conducted under laboratory atmosphere and of exposure to the laboratory atmosphere during sample transportation from the drying system to the combustion oven are confirmed. These results are very encouraging, as all participants obtained OBT activity results, which are in good agreement with each other.

### INTRODUCTION

In the 1960s, tritium levels in the Northern Hemisphere's environment were closely related to the atmospheric testing of nuclear weapons. Since the nuclear test ban treaty, environmental tritium levels are slowly returning to their pre-bomb testing level. Therefore, the main anthropogenic sources are now related to nuclear facility releases into the surrounding environment. Tritium occurs in environmental samples in 3 forms: as tissue-free water tritium (TFWT) (i) and within living organisms, where it may label the organic matter either as exchangeable organically bound tritium (ii) or non-exchangeable organically bound tritium (iii). Component (i) is easily removed by evaporation at low temperature or by freeze-drying, and is in the form of tritiated water. Component (ii) tritium is exchangeable with the system's water to varying degrees, depending on the molecular structure. It is designated as exchangeable OBT (E-OBT). Type (iii) tritium is on the contrary tightly held by the organic structure, hence its designation as non-exchangeable (NE-OBT).

To monitor tritium bioaccumulation in environmental samples, the sensitivity and accuracy of the analytical procedure are of primary importance. When considering environmental samples, the tritium activity of several fractions can be measured. Namely, the total amount that can be divided between the free water and the OBT fraction, the latter possibly separated between exchangeable and non-exchangeable OBT (Ware and Allott 1999). At present, regular legally required monitoring is carried out based on water and on environmental samples (mainly grass and milk) for which tissue-free water tritium (TFWT) is measured. However, no OBT assessments are included in these

obligatory analyses, and very few intercomparison exercises have been organized since that of Atomic Energy Canada Limited (AECL) (Workman et al. 2005). Nevertheless, over the past few years, interest has been focused on OBT, which may be of greater radiological importance (Inoue et al. 1992; Diabate and Strack 1993; Choi et al. 2005). Moreover, the data relative to OBT concentrations in environmental samples is scarce and difficult to compare, as the fractions measured could be different (Vichot et al. 2008). Indeed, to analyze any tritium fraction in an environmental sample, the suitable analytical procedure has to be used (Baglan et al. 2005). Such procedures are now employed by several laboratories in charge of environmental tritium monitoring or carrying out research on tritium behavior in the biosphere.

An intercomparison exercise was therefore prepared by the CETAMA to assess laboratories' capabilities for OBT determination. To avoid any misinterpretation of the results, all participating facilities were asked to determine the OBT activity in the sample delivered to them. The chosen matrix was grass that was sampled on the same day from a single location, prior to homogenization. The grass was then divided into 2 aliquots: (i) fresh, which was homogenized, sealed under vacuum, and sent to the analytical laboratories; and (ii) dry, which was processed in a single laboratory prior to being sent to the participants.

The results obtained are primary elements in further enhancing the accuracy of experimental data for OBT activities in environmental samples, and could be of importance in improving the input data used to compute tritium impact.

## **EXPERIMENTAL PROCEDURE**

### **Participants**

Eleven laboratories, numbered from 1 to 11, were registered for this exercise. Six returned data for the fresh aliquot, and 8 for the dry sample. Their results are hereafter marked as lab number-1 and lab number-2, respectively, for the fresh and dry aliquots.

### **Sampling and Packaging**

The samples were collected inside a French reprocessing plant zone where tritium is handled during the reprocessing process. The sampling site was chosen by the site's environmental monitoring laboratory to ensure sufficient activity for intercomparison purposes. The chosen sample was grass, owing to the ease of sampling and also its availability.

A total amount of about 15 kg of grass was collected and divided into 2 aliquots (Figure 1) after homogenization. The fresh aliquot was sent directly to the participating laboratories after freezing, while the material for the dry sample was sent to a laboratory that carried out the drying prior to transfer to the other laboratories. The lyophilization device used to prepare the dry aliquot was a Heto Drywinner (THERMO Eletron Corporation).

### **Sample Analysis**

All laboratories received 2 aliquots of the grass sample, 1 fresh and 1 dry. The general flowsheet used to perform the analysis is summarized in Figure 2. On reception, the fresh aliquot was dried by the participating laboratories. After the drying stage, the sample was prepared for measurement using a suitable analytical procedure. Measurement was mainly performed with liquid scintillation counting, as only 1 lab used  $^3\text{He}$  detection via mass spectrometry.

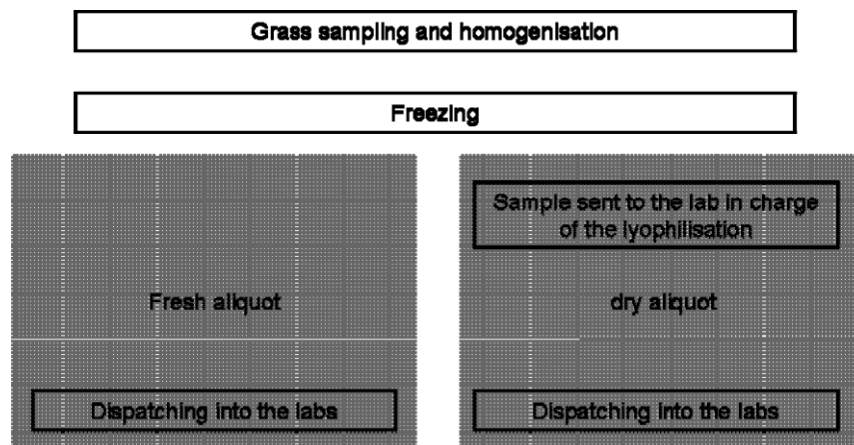


Figure 1 Sample pretreatment

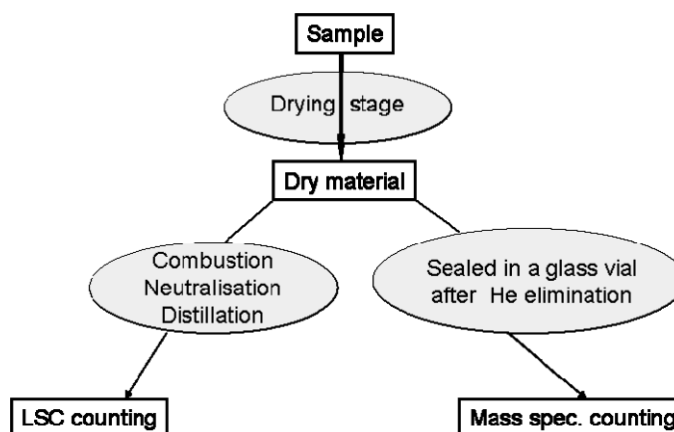


Figure 2 Sample analytical scheme

The drying stage was performed by lyophilization. The total removal of water was confirmed by weighing residual samples. Special attention was given to the washing of the freeze-drying chambers, and tests were performed to ensure the absence of contamination. Then, depending of the analytical tool, the dry sample was burned in a special oven (i) or sealed in a glass vial after helium purging (ii). The principle of the combustion apparatus has already been described in the literature (Takashima et al. 1987; Pointurier et al. 2004). A quartz tube goes through the 2 heating zones of the oven (Figure 3). In the first zone, the sample is held in a quartz vessel containing 5 to 50 g of dry sample, depending on the tube diameter. The part of the quartz tube that is inside the second heating zone contains catalyst to oxidize combustion gases. The temperatures of both zones are independently adjustable, and the 1st heating zone is mobile. The quartz vessel containing the sample is placed just before the 1st heating part, so that the leading edge of the sample is heated by the furnace. When the sample starts to ignite, a flame appears at the extremity of the sample and the heating unit is moved towards the sample so that the flame moves slowly across the whole sample. The 2nd heating zone is fixed and held at a constant temperature of  $850 \pm 20$  °C. The combustion gases, swept over the catalyst by a stream of pure oxygen, are oxidized by the catalyst and the water vapor trapped in the cold trap. Only a small part of the water vapor escapes from the trap and is absorbed

by a desiccant trap at the cold trap exit. At the end of combustion, the glassware containing the frozen combustion water is removed from the combustion apparatus and immediately closed with appropriate caps.

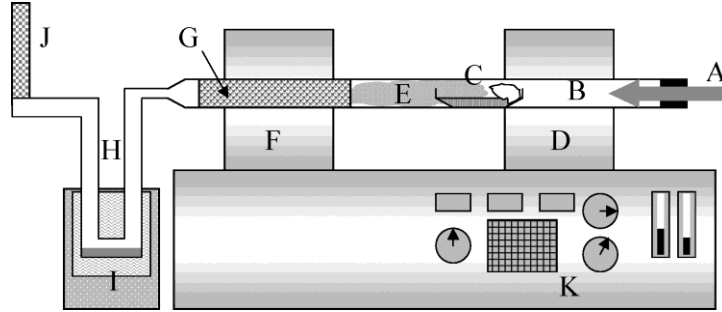


Figure 3 Combustion oven. A: dry and pure oxygen flux; B: quartz tube; C: sample; D: first heating unit (mobile); E: combustion gases; F: second heating unit (fixed); G: catalyst with quartz bead; H: "U" tube for water vapor trapping; I: cold trap; J: desiccant; K: controllers.

However, the combustion water is not directly suitable for liquid scintillation counting due to its acidity and the various impurities also collected in the cold trap. Therefore, the water was neutralized and a distillation performed under atmospheric pressure using conventional laboratory glassware.

For the combustion step, an alternative to the combustion oven is to employ an oxidizer. In this case, a very small amount of sample (<1 g) is placed in the combustion cone prior to introduction into the oxidizer. After combustion, the water recovered is condensed and added automatically to the mixture. The combustion yield is estimated under the same conditions, using a tritium standard.

The main drawback of this technique lies in the low amount usable (<1 g), which leads to high detection limits not suited for environmental purposes. However, it exhibits a strong potential as a screening tool due to its rapidity.

Tritium determination in combustion water is performed through liquid scintillation counting, a well-established and documented technique (Birks 1964; Horocks 1974), using the following equation:

$$A_b = \frac{(n - n_0)}{60 \times \eta \times b} \quad (1)$$

where  $b$  is the mass (kg) or the volume (L) of combustion water in the counting vials;  $n$  is the counting rate for the sample (cpm);  $n_0$  is the counting rate for the associate blank sample (cpm); and  $\eta$  is the counting yield (dimensionless number between 0 and 1).

The relative expanded uncertainty in the result is given with a coverage factor of 2:

$$\frac{u_c(A_b)}{A_b} = 2 \times \sqrt{\frac{\frac{n}{t} + \frac{n_0}{t_0}}{\left(\frac{n}{t} - \frac{n_0}{t_0}\right)^2} + \left(\frac{u_c(b)}{b}\right)^2 + \left(\frac{u_c(\eta)}{\eta}\right)^2} \quad (2)$$

where  $t$  is counting time for the sample (min) and  $t_0$  is the counting time for the associated blank sample (min).

For environmental samples, the values obtained in Bq/kg or L of combustion water have to be converted into Bq/kg sample (dry or fresh). For OBT, the equations are:

$$A_d^{OBT} = \frac{A_b \times (\%_H \text{ sample})}{(\%_H \text{ water})} \text{ for the dry material} \quad (3)$$

and

$$A_f^{OBT} = \frac{A_d^{OBT} \times m_d}{m_f} = \frac{A_b \times (\%_H \text{ sample}) \times m_d}{(\%_H \text{ water}) \times m_f} \text{ for the fresh material} \quad (4)$$

where  $A_d^{OBT}$  is the activity of the OBT per kg of dry sample;  $A_f^{OBT}$  the activity of the OBT per kg of fresh sample;  $m_f$  is the fresh sample mass; and  $m_d$  is the dry sample mass.

The expanded uncertainty on the result is given with a coverage factor of 2:

$$U_{A_d^{OBT}} = 2 \times A_d^{OBT} \times \sqrt{\left(\frac{u_{A_b}}{A_b}\right)^2 + \left(\frac{u_{(\%_H \text{ sample})}}{(\%_H \text{ sample})}\right)^2 + \left(\frac{u_{(\%_H \text{ water})}}{(\%_H \text{ water})}\right)^2} \quad (5)$$

$$U_{A_f^{OBT}} = 2 \times A_f^{OBT} \times \sqrt{\left(\frac{u_{A_d}}{A_d}\right)^2 + \left(\frac{u_{m_d}}{m_d}\right)^2 + \left(\frac{u_{m_f}}{m_f}\right)^2} \quad (6)$$

These equations were used by the participants measuring tritium by liquid scintillation during the exercise.

Tritium was measured using the helium-3 ingrowth method (developed by Clarke et al. 1976) for water samples. The principle of the method is to remove the atmospheric  $^3\text{He}$  initially present in the sample by degassing under high vacuum, and then to store it in a closed container (usually a low He-diffusivity glass bulb) to allow for the accumulation of tritiumgenic  $^3\text{He}$ . The tritium content of the sample is subsequently deduced from the mass spectrometric determination of the amount of  $^3\text{He}$  produced during the storage time. Since helium diffusivity is very high in organic compounds, allowing the tritiumgenic  $^3\text{He}$  to diffuse out of the biological tissues and to accumulate in the storage container, there is no obstacle to applying this highly sensitive technique for measuring tritium to environmental samples. The samples were analyzed using the procedure detailed by Jean-Baptiste et al. (1992). Briefly, each sample is put in a Corning 1724 glass bulb and pumped down to  $10^{-5}$  Torr. Then, the bulb is flame-sealed and stored at  $-20$  °C in a freezer for  $^3\text{He}$  ingrowths. Although Corning 1724 glass was selected for its low helium diffusivity, the low temperature is intended to further reduce  $^3\text{He}$  diffusion through the glass wall during storage. After a sufficient storage time, the bulb is placed on the inlet line of a MAP 215-50 noble gas mass spectrometer and reopened by breaking its tip with a special pneumatic actuator.  $^3\text{He}^+$  ions are detected on an electron multiplier operated in the pulse mode. The  $^3\text{He}$  blank ( $<10^{-19}$  mol), which is almost entirely due to the residual helium dissolved in the sample after pumping, is deduced from the measurement of  $^4\text{He}$  applying the atmospheric helium isotopic ratio:  $^3\text{He}/^4\text{He} = 1.38 \times 10^{-6}$ .

The T/H value of the sample is deduced from the measured amount of tritiumgenic  $^3\text{He}$  (in mol) following the formula:

$$\frac{T}{H} = \frac{{}^3\text{He}}{(m \times [H] \times (1 - e^{-\lambda t}))} \quad (7)$$

where  $m$  is the mass of the sample (in kg),  $[H]$  is its hydrogen content (in mol/kg),  $\lambda$  is the decay constant of tritium, and  $t$  is the storage time. The hydrogen content of each sample was measured on a CHN analyzer at the Micro-analysis Laboratory (CNRS/ICSN, Gif sur Yvette). All measurements were made against an atmospheric air standard ( $^4\text{He} = 5.24$  ppm,  $^3\text{He}/^4\text{He} = 1.38 \times 10^{-6}$ ). Overall relative uncertainty on the tritium determination was better than 5%.

### Statistical Processing Methods

The statistical tests classically used to interpret the results of a round-robin refer to a population meeting the criteria of a normal distribution defined by the mean and the variance. To check this specific point, the Shapiro-Wilk test was used for both aliquots. However, the insufficient number of measurements and/or the presence of abnormal values reported in this round-robin led to the use of robust statistical methods for which no hypothesis concerning the distribution is necessary. These methods take into account all the results, including those considered abnormal according to normal distribution criteria: none of the results are disregarded in calculating the mean and standard deviation. These methods based on calculation algorithms described in standards ISO 5725-6 and ISO/DIS 13528 allow the determination of the robust means, and of the reproducibility and repeatability standard deviations. The objective of the following calculations is to estimate the standard deviations of repeatability ( $s_r$ ) and reproducibility ( $s_R$ ). Repeatability implies that the measurements are performed by the same operator with the same instrument using a single method within a short time period to obtain results under conditions as similar as possible. Reproducibility conditions occur when any of these conditions changes: operator, instrument, method variant, time frame, or any other cause of variability. The results obtained can therefore be used to calculate the standard deviation of repeatability (or intralaboratory reproducibility), which measures the scattering of the results obtained in 5 independent tests by each laboratory, and the standard deviation of interlaboratory reproducibility, which measures the scattering of the mean results obtained by all the laboratories.

To compare the results obtained for the 2 aliquots, a general approach was adopted. This meant first checking for outliers (Grubbs, Dixon), discarding results that were not obtained under repeatability conditions within a single laboratory, homoscedasticity (Fisher), then verifying the null hypothesis: that the mean values for each aliquot are equal (Student). Moreover, the repeatability ( $r = k\sqrt{2} s_r$ ) and reproducibility ( $R = k\sqrt{2} s_R$ ) limits were determined.

### RESULTS AND DISCUSSION

Depending on their analytical means, the various laboratories used experimental or tabulated values for the hydrogen percentage in the sample. The mean experimental value,  $\%H_m = 6.2 \pm 0.2\%$ , is characterized by a scattering low enough to have only a very slight impact on the activity values determined.

Among the data given by the facilities for the 2 aliquots, the mean and standard deviation associated with the fresh to dry mass ratio ( $R_m$ ) and the water content ( $W$ ) were determined:  $R_m^{\text{fresh}} = 3.41 \pm 0.06$  and  $R_m^{\text{dry}} = 3.47 \pm 0.12$ ;  $W^{\text{fresh}} = 70.64 \pm 0.55\%$  and  $W^{\text{dry}} = 71.01 \pm 1.30\%$ . The values thus obtained are consistent, and also with those known for grass samples.

Moreover, 2 guideline values, the ratio for the combustion water recovered from the burned dry sample compared to the combustion yield were followed throughout the combustion stage to assess any departure from standard conditions. For all the participating laboratories, these values remained normal, i.e. around 50% for the combustion water to burned sample ratio and 90% for the combustion yield.

The consistency of all these technical parameters for all the different participants showed that the analytical tools are efficient. For both aliquots, the activity results are only given for the combustion water and the dry material, as those for the fresh material were derived from the previous one (Equation 4). Moreover, the main statistical results including consensus values (NF ISO 13528) are summarized for the various fractions.

### Fresh Aliquot

The treatment to perform OBT analysis is more tedious for this aliquot, which led to a lower participation with only 4 facilities giving results for the combustion water (Figure 4) and 6 for the dry material (Figure 5).

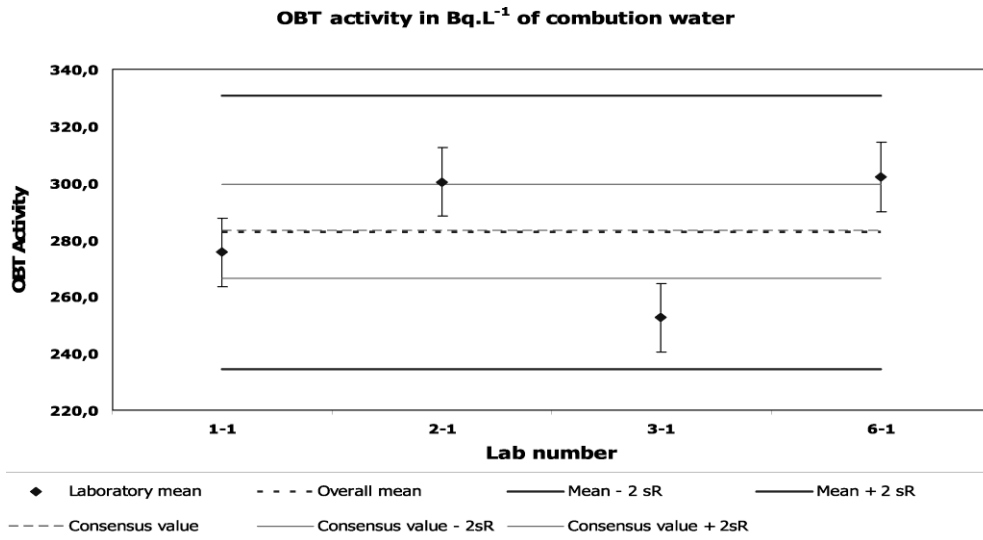


Figure 4 OBT activity in Bq L<sup>-1</sup> of combustion water for the fresh aliquot

The results reported for the combustion water are close to the consensus value and lie within the reproducibility limit (-17 to +17%). The results reported for the dry mass are also close to the consensus value and most lie within the reproducibility limit (-19 to +19%). The larger interval in terms of reproducibility may originate from:

- The use by laboratory 6 of a hydrogen percentage value from the literature lower than that actually observed in the sample, which would explain the relative position of the laboratory mean regarding the consensus value for the 2 fractions;
- The presence of a new laboratory whose results exhibit higher scattering due to the analysis of very low amounts, leading to an increased influence of the counting statistic.



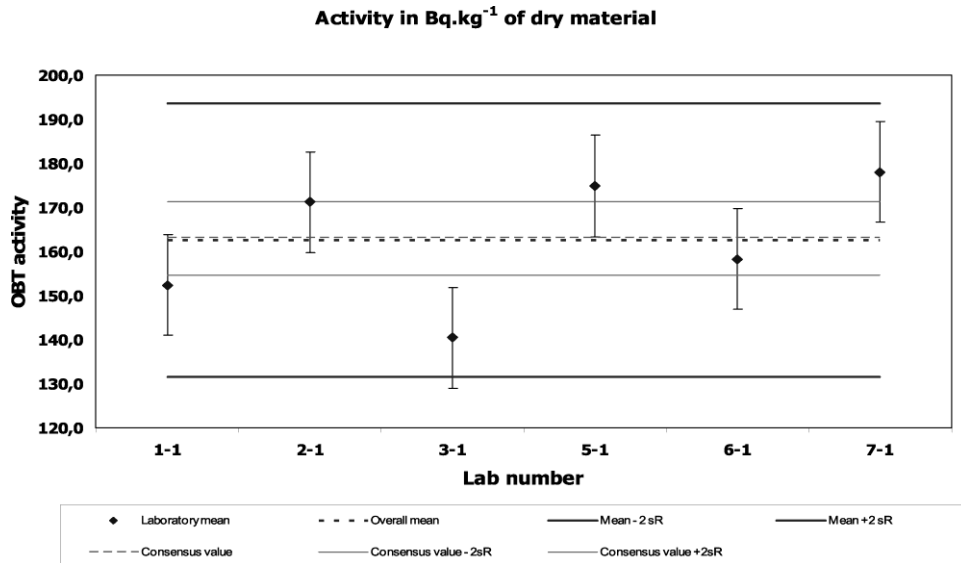


Figure 5 OBT activity in Bq.kg<sup>-1</sup> of dry material for the fresh aliquot

### Dry Aliquot

The treatment necessary to perform OBT analysis is shorter for this aliquot; therefore, 6 laboratories gave results for the combustion water (Figure 6) and 8 for the dry material (Figure 7).

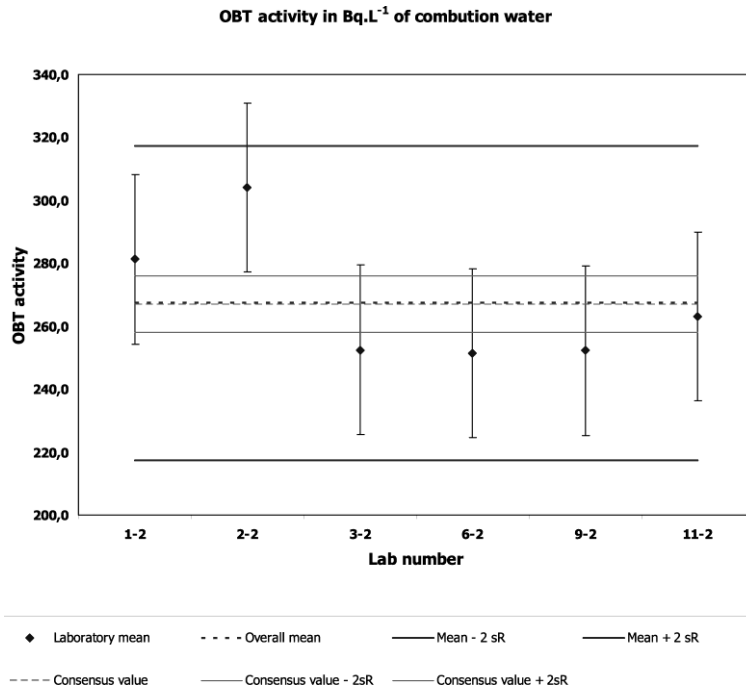


Figure 6 OBT activity in Bq.L<sup>-1</sup> of combustion water for the dry aliquot

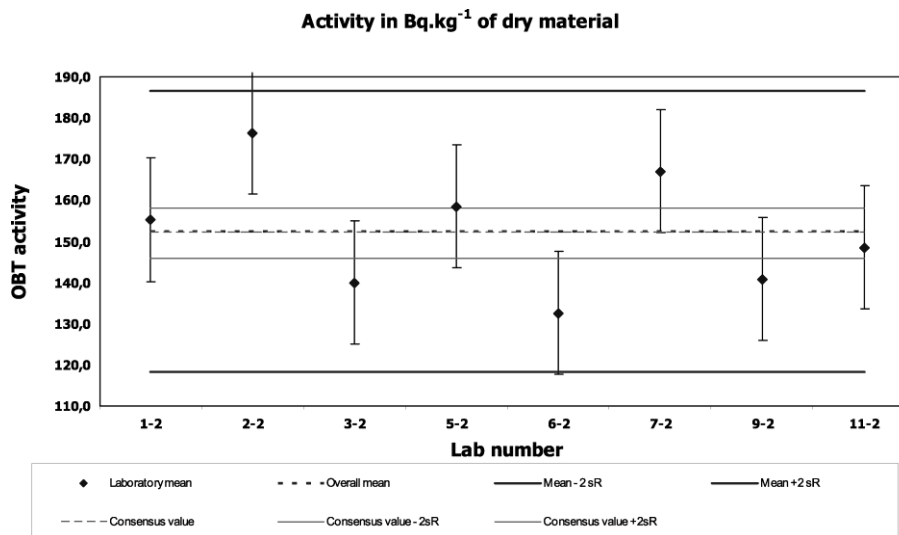


Figure 7 OBt activity in Bq kg<sup>-1</sup> of dry material for the dry aliquot

The results reported for the combustion water are close to the consensus values and lie within the reproducibility limit (−19 to +19%). However, the scattering of the values is larger than that observed for the fresh aliquot. Two hypotheses could explain this behavior: the use of the robust method, in which outliers are not rejected; and the fact that 1 laboratory did not meet the repeatability criteria for the 5 replicates that were used.

The results reported for the dry mass are also close to the consensus value and most lie within the reproducibility limit (−22 to +22%). The origins of the wider interval in term of the reproducibility may combine the reasons given for the fresh aliquot on the dry material and those previously explained regarding combustion water.

## DISCUSSION

All the results are summarized for both aliquots (Table 1) of the grass sample. At first glance, the observed means using robust methods seem to be lower for the dry aliquots. However, it is difficult to reach straightforward conclusions, as for the various aliquots the results are always found within the reproducibility limits. Under these conditions, it is obvious that the scattering of the results would be further reduced by sampling larger amounts to avoid any counting statistic impact, both by limiting the influence of environmental conditions on the value of the hydrogen percentage and by decreasing interlaboratory scattering. Nevertheless, the values obtained by all the laboratories meet the reproducibility criteria, underlining the progress made since the first exercise, when the reproducibility standard deviations were between 50 and 80%.

However, as both aliquots came from the same grass sample, the results obtained should be identical. To check the  $H_0$  hypothesis, i.e. that the determined means are identical for both aliquots, suitable statistical tests were performed. The means determined for the 2 aliquots were compared for the different laboratories, using only the values obtained under repeatability conditions within each facility. As the values in Bq kg<sup>-1</sup> of fresh material were derived from those of dry material (Equation 4) by a simple mass ratio, only the activities in Bq kg<sup>-1</sup> of combustion water (i) and dry material (ii) were taken into account:

Table 1 Round-robin summary.

Activity per kg or L	Fresh aliquot			Dry aliquot		
	Combustion water (Bq L <sup>-1</sup> )	Dry material (Bq kg <sup>-1</sup> )	Fresh material (Bq kg <sup>-1</sup> )	Combustion water (Bq L <sup>-1</sup> )	Dry material (Bq kg <sup>-1</sup> )	Fresh material (Bq kg <sup>-1</sup> )
Number of participating labs	4	6	6	6	8	8
Data	20	30	30	26	35	35
Grand mean	282.8	163.1	47.7	266.5	151.8	43.8
s <sub>r</sub>	6.7	4.7	1.6	10.1	6.4	2.0
s <sub>R</sub>	27.4	18.1	4.5	24.6	17.1	4.1
r	18.9	18.1	4.4	28.6	13.3	5.5
R	78.6	48.4	12.7	69.6	51.2	11.7
consensus value	<b>283 ± 16</b>	<b>163 ± 8</b>	<b>48 ± 4</b>	<b>267 ± 9</b>	<b>152 ± 6</b>	<b>44 ± 4</b>

- (i) The population is small ( $n < 30$ ); therefore, the homoscedasticity of the variance ( $F$  test) was checked prior to carrying out a  $t$  test, to verify that the means were equal.
- (ii) The population is large enough to do the  $t$  test directly.

The experimental values were then compared to that found in the literature (Neuilly 1999; Sokal and Rohlf 1998) (Table 2).

Table 2 Mean comparison.

	Test	Experimental value	Discriminating value ( $\alpha = 5\%$ )	Conclusions
Bq kg <sup>-1</sup> of combustion water	Fisher	0.85	2.08	Homogeneity of the variance
Bq kg <sup>-1</sup> of combustion water	Student	1.74	2.02	Identical mean
Bq kg <sup>-1</sup> of dry material	Student	1.91	2.00	Identical mean

For the combustion water, both experimental values were lower than the discriminating value, which demonstrates the homogeneity of the variance for a risk chosen equal to 5%, and confirm the  $H_0$  hypothesis. For the dry grass, the experimental value is lower than the discriminating value, leading to the same conclusion. These results confirm that the drying stage was performed well by the laboratories. However, the hydrogen percentage value can play a role, especially when literature data are used. Indeed, very little data is available, which means it is not completely representative of environmental variability. Therefore, experimental assessment of this important parameter is recommended.

As both sets of values are identical, a consensus value for the grass sample itself could be obtained by calculating the weighted mean and the associated uncertainty for each fraction (Table 3).

Table 3 Consensus values and associated uncertainties ( $k = 2$ ) for the analyzed grass.

Fraction	Activity (Bq kg <sup>-1</sup> )	Uncertainty (Bq kg <sup>-1</sup> )
Combustion water	274	12
Dry material	157	7
Fresh material	46	4

Nevertheless, to prepare certified reference material, the following are needed:

- Larger samples, as 15 kg is only just enough for the purpose of such a round-robin exercise;
- A guarantee of sample stability over a time period long enough to ensure the usefulness of such material; rather difficult criteria for  $^3\text{H}$ .

It is known that isotopic exchange with hydrogen present in the atmosphere can modify the amount of tritium in the sample (Belot et al. 1996), even when it is stored in a freezer (where the exchange is very much slower, but not halted).

## CONCLUSION

In order to assess and improve the performances of several laboratories dealing with OBT determination, an intercomparison exercise was organized by the CETAMA. The results obtained are very encouraging, as most of the differences observed can be explained by variations in the experimental conditions. Nevertheless, the scattering observed for each facility is consistent with this round-robin repeatability limit, and with the reproducibility limit when considering all the values. Therefore, consensus values are proposed for the dry and fresh aliquots. As they came from the same grass sample, the determined mean activities should be identical. This hypothesis was assessed using suitable statistical tests, which allowed a consensus value to be proposed for each fraction, namely  $274 \pm 12 \text{ Bq kg}^{-1}$  for the combustion water,  $157 \pm 7 \text{ Bq kg}^{-1}$  for the dry grass, and  $46 \pm 4 \text{ Bq kg}^{-1}$  for the fresh material.

The results confirm that several stages of the process, such as the drying and the measurement, are performed well by the participating laboratories. However, the use of literature data for the hydrogen percentage employed to convert activity values from  $\text{Bq kg}^{-1}$  for the combustion water to  $\text{Bq kg}^{-1}$  of dry material may have a negative influence on the activity results. Indeed, environmental variations are not correctly matched using this data, and an experimental determination is therefore recommended.

As part of its objective regarding validated analytical procedures for OBT determination, the CETAMA will organize a new exercise next year. Simultaneously, a tentative assessment of the mathematical relation  $T_{\text{total}} = \text{HTO} + \text{OBT}$  will be performed. From these exercises, an analytical procedure for OBT and NE-OBT determination will be proposed for validation, to obtain environmental Certified Reference Materials for future OBT determination.

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