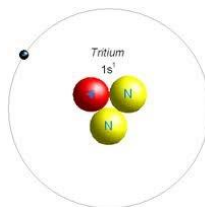


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## 9<sup>th</sup> OBT Workshop

May 10<sup>th</sup>-12<sup>th</sup> 2023  
Antwerp, Belgium

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# The 6<sup>th</sup> Organically Bound Tritium (OBT) Inter-laboratory Exercise

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# Contents



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## 6<sup>th</sup> OBT Intercomparison exercise

1. Preliminary activities

2. Registration of the participants and schedule

3. Sample preparation

4. HTO analysis

5. Sample combustion for OBT analysis

6. Evaluation of the results

7. Conclusions

# The 6<sup>th</sup> OBT Intercomparison exercise



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## 1. Preliminary activities:

- Type of sample: **fruits – Quinces (*Cydonia oblonga*)** – was chosen at the 7<sup>th</sup> OBT Workshop, in Toronto – Canada, in September 2018;
- Sampling location: Environmental Laboratory yard – **Cernavoda town** (about 2 km from the Cernavoda NPP);
- Reference date: **23 October 2018.**



# The 6<sup>th</sup> OBT Intercomparison exercise



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## 2. Registration of the participants and schedule:

- Registration deadline: 31<sup>st</sup> December 2018; 31 laboratories from 11 countries were registered: Belgium (1), Canada (5), China (4), Croatia (1), France (9), Hungary (1), Japan (4), Korea (1), Romania (2), Slovenia (1), United Kingdom (2).
- Sample dispatch: March – May 2019;
- Reporting deadline: 31<sup>st</sup> July 2017 (extended for some labs).

## 3. Sample preparation:

- Quantity: about 50 kg fresh sample; 150 g of dehydrated sample/ laboratory;
- Oven drying; Mill cutting; Homogenization; Determination of Hydrogen % on dehydrated sample; Sealing subsamples; Phytosanitary certificate (for Japan).



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## 4. HTO analysis:

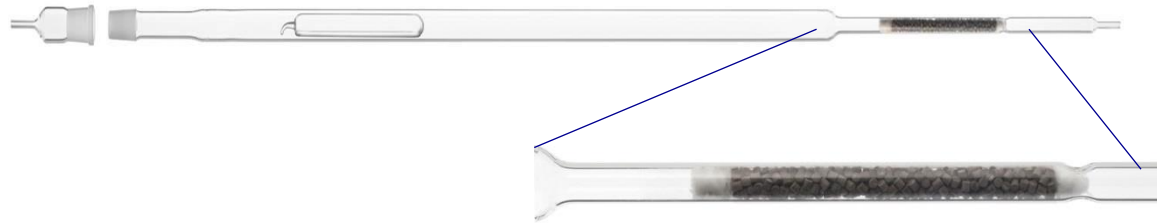
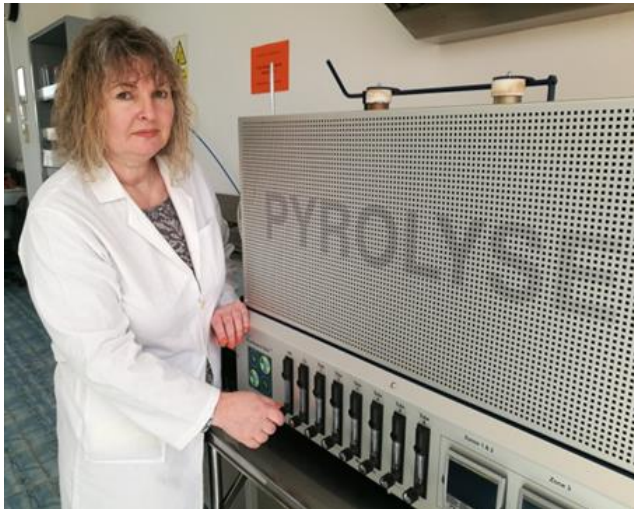
- Sample preparation: extracting free water by azeotropic distillation with toluene; mixing 8 ml HTO : 12 ml of Ultima Gold LLT cocktail in 20 ml PE vials;
- Analysing systems: Tri-Carb 3180 TR/SL;
- Fresh to dry mass ratio: 6.2 (16% dry mass; 84% dehydration water)
- Hydrogen percentage in dehydrated sample (H%):  
 **$m \pm 2s = 5.71 \pm 0.12 \%$**  (ICSI-Rm. Valcea)
- HTO activity in free water:  **$44 \pm 3 \text{ Bq/L}$**  (k=2)
- HTO activity in fresh sample:  **$37 \pm 3 \text{ Bq/kg}$**  (k=2)



# The 6<sup>th</sup> OBT Intercomparison exercise

## 5. Sample combustion for OBT analysis:

- Pyrolyser-6 Trio System from Raddec:
  - 6-tubeTri-zone, Eurotherm 3504 and Nanodac controllers, AGS (automated gas changing);
  - Pt-alumina catalyst (10g/tube), Quartz wool;
  - Heating profile: from 50 – 800°C in 6 steps; air and Oxygen;
  - 5 g of dehydrated sample/ tube;
  - 1.5 – 1.8 g of combustion water trapped direct to 20 ml PE vials;
  - 10 ml Ultima Gold cocktail/ vial.



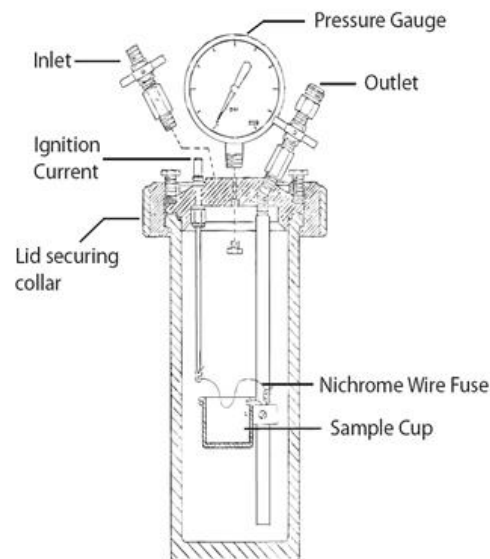
# The 6<sup>th</sup> OBT Intercomparison exercise



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## 5. Sample combustion for OBT analysis:

- Parr 1121 Oxygen Calorimeter:
  - 1850 ml pressure vessel; Ni-Chrome wire fuse; oxygen;
  - 20 g of dehydrated sample/cup;
  - 10 g of combustion water recovered;
  - Distillation of combustion water with Na<sub>2</sub>CO<sub>3</sub> (sodium carbonate) and Na<sub>2</sub>O<sub>5</sub>S<sub>2</sub> (sodium thiosulphate);
  - 8 ml distilled water : 12 ml Ultima Gold LLT cocktail.



# The 6<sup>th</sup> OBT Intercomparison exercise

## 5. Sample combustion for OBT analysis:

- Sample Oxidizer-307 from Perkin-Elmer:
  - Automated system; Nitrogen and Oxygen gas;
  - 1.2 g of dehydrated sample/ combusto-cone;
  - 2.5 minutes combustion time;
  - Combustion water trapped directly in 20 ml glass vial with 15 ml Monophase S cocktail.





# The 6<sup>th</sup> OBT Intercomparison exercise



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## 6. Evaluation of the results:

- SNN-Cernavoda NPP, Environmental Laboratory analysed the samples in a Tri-Carb 3180 TR/SL – results for the 6<sup>th</sup> OBT Inter-comparison exercise:

Dehydrated sample mass [g]	Water of combustion mass [g]	OBT_woc [Bq/L]	2u [Bq/L]	OBT_dehy [Bq/kg]	2u [Bq/kg]
<b>Parr 1121</b>					
20.63	9.1572	49.83	2.49	25.61	1.28
20.87	9.6866	50.24	2.51	25.82	1.29
20.64	9.9558	51.47	2.57	26.45	1.32
20.58	9.6900	53.22	2.66	27.35	1.37
20.72	9.9322	50.79	2.54	26.10	1.31
<b>Average</b>	<b>20.69</b>	<b>9.68</b>	<b>51.11</b>	<b>2.55</b>	<b>26.27</b>
<b>Pyrolyser-6</b>					
5.07	1.6422	57.24	2.86	29.42	1.47
5.03	1.6421	57.85	2.89	29.73	1.49
5.07	1.6993	59.24	2.96	30.44	1.52
5.01	1.7329	57.71	2.89	29.66	1.48
5.04	1.4726	58.63	2.93	30.13	1.51
<b>Average</b>	<b>5.04</b>	<b>1.64</b>	<b>58.13</b>	<b>2.91</b>	<b>29.87</b>

# The 6<sup>th</sup> OBT Intercomparison exercise



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## 6. Evaluation of the results (cont.):

- Results were reported for the first time in excel file: 28 labs reported of 31 labs registered;
- Some labs didn't have 5 replicates; 1 lab has just 1 replicate; 1 lab didn't report the uncertainties of the measurements; some labs used 2 methods;
- Some labs reported only OBT\_woc [Bq/L] or only OBT\_dehydrated sample [Bq/kg]; 1 lab protected the reporting form; 1 lab modified the reporting form;
- Evaluated results: 27 for OBT\_woc [Bq/L]; 30 for OBT\_dehydrated sample [Bq/kg];
- Many labs used combustion furnace (13 labs); 4 labs used Pyrolyser-6 trio; 1 lab used Hyperbaric Oxidizer; 1 lab used Oxidizer 307; 7 labs used Parr 1121; 2 labs used He-ingrowth method;
- Many labs measured the sample in Quantulus LSC (17 labs); some labs used Tri-Carb LSC (8 labs); some labs used Hitachi LSC (4 labs); 2 labs used He Mass Spectrometer; and 1 lab used Aloka LSC.

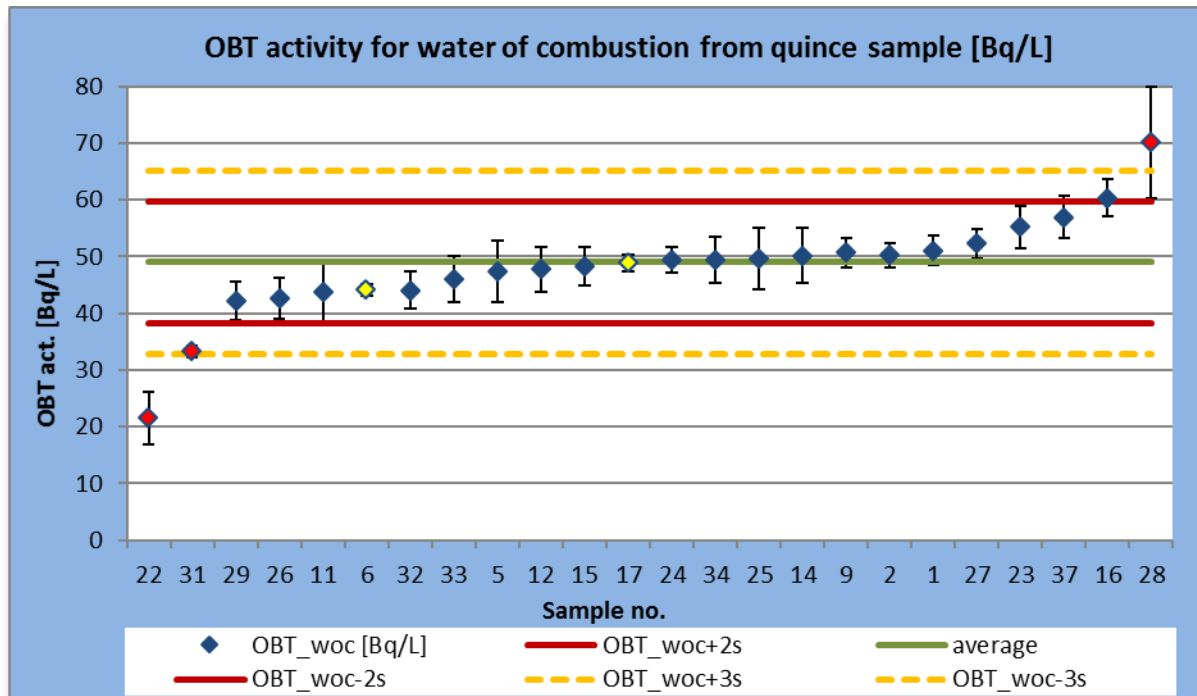
# The 6<sup>th</sup> OBT Intercomparison exercise



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## 6. Evaluation of the results (cont.):

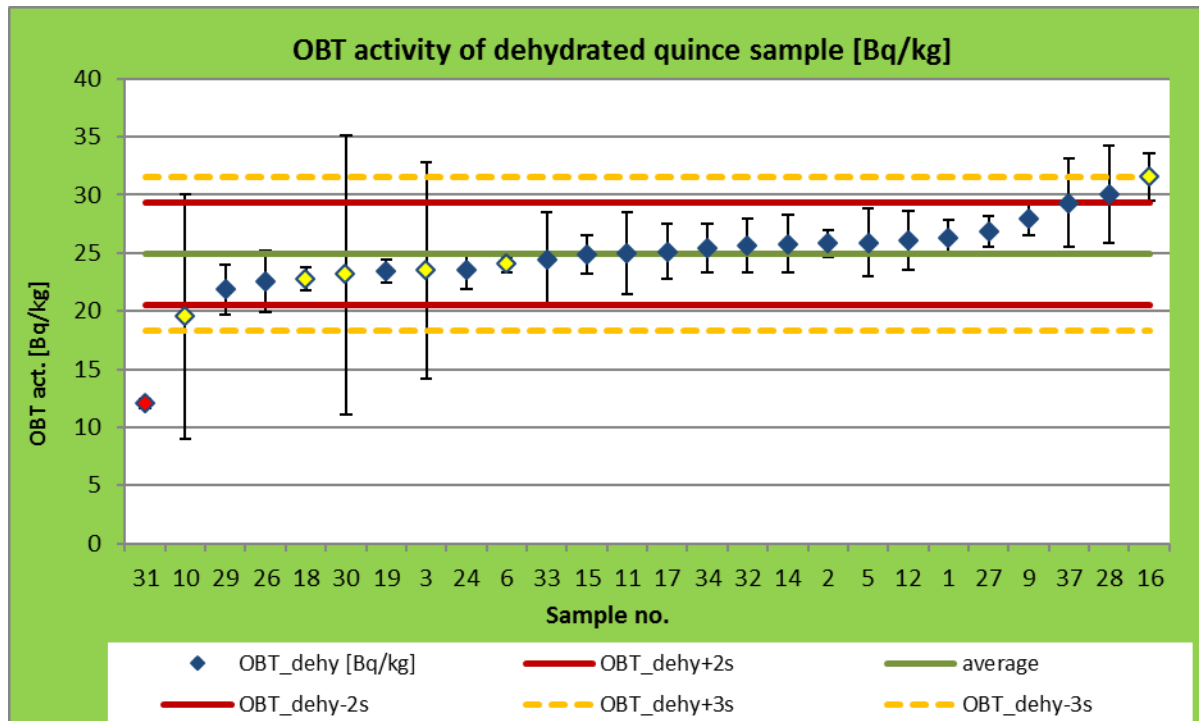
- Results of Sample#4 were excluded because the laboratory did not provide the corresponding uncertainties. On the other hand, for calculating repeatability and reproducibility standard deviation, the results of 3 labs (Sample #31 for activity of dehydrated quince and Sample #22, #28 and #31 for activity of combustion water) were excluded after an outlier test was conducted based on each lab's average OBT value of the 5 replicated measurements and also based on the Zeta score.
- OBT activity with all data: **21.4 Bq/L to 70.1 Bq/L**
- OBT activity without outliers: **42.1 Bq/L to 60.4 Bq/L**



# The 6<sup>th</sup> OBT Intercomparison exercise

## 6. Evaluation of the results (cont.):

- OBT activity with all data: **12.1 Bq/kg to 31.5 Bq/kg**
- OBT activity without outliers: **19.5 Bq/kg to 31.5 Bq/kg**
- Hydrogen % experimental values reported: **5.7% to 6.46 %**
- Hydrogen % provided in the reporting form: **5.71 ± 0.12 %** (ICSI, Râmnicu Vâlcea, Romania)



# The 6<sup>th</sup> OBT Intercomparison exercise



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## 6. Evaluation of the results (cont.):

- Assigned values – robust analysis (Algorithm A), ISO 13528:2015

Assigned value			
Approach	Bq.L <sup>-1</sup>	Standard deviation s(Xpt) or S*	Standard uncertainty u(Xpt)
Arithmetic mean (all data)	48.1	2.1	
Arithmetic mean (excluding outliers)	49.1	1.8	
Median	49.2	1.5	
Robust analysis (Algorithm A)	48.6	5.4	1.4

Assigned value			
Approach	Bq.kg <sup>-1</sup>	Standard deviation s(Xpt) or S*	Standard uncertainty u(Xpt)
Arithmetic mean (all data)	24.7	1.5	
Arithmetic mean (excluding outliers)	25.2	1.5	
Median	25.1	0.8	
Robust analysis (Algorithm A)	24.9	2.2	0.5

s\* - robust standard deviation

The standard uncertainty on the assigned value is  $< 0.3\sigma$  and is therefore considered negligible.

# The 6<sup>th</sup> OBT Intercomparison exercise



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## 6. Evaluation of the results (cont.):

- Evaluation criteria

Criteria	% deviation	Z score	Zeta score	Uncertainty
Calculation	$D_i = \frac{(x_i - x_{pt})}{x_{pt}} \times 100$	$z = \frac{(x_i - x_{pt})}{s^*}$	$\zeta_i = \frac{(x_i - x_{pt})}{\sqrt{u^2(x_i) + u^2(x_{pt})}}$	$u_{min} = u(x_{pt})$ $u_{max} = 1.5s^*$
Pass criteria	$(x_{pt} + 3s^*) > D_i > (x_{pt} - 3s^*)$	$ z  < 2$ – PASS $2 <  z  < 3$ – CHECK $ z  > 3$ – FAIL	$ \zeta  < 2$ – PASS $2 <  \zeta  < 3$ – CHECK $ \zeta  > 3$ – FAIL	$u_{min} < u(x_i) < u_{max}$

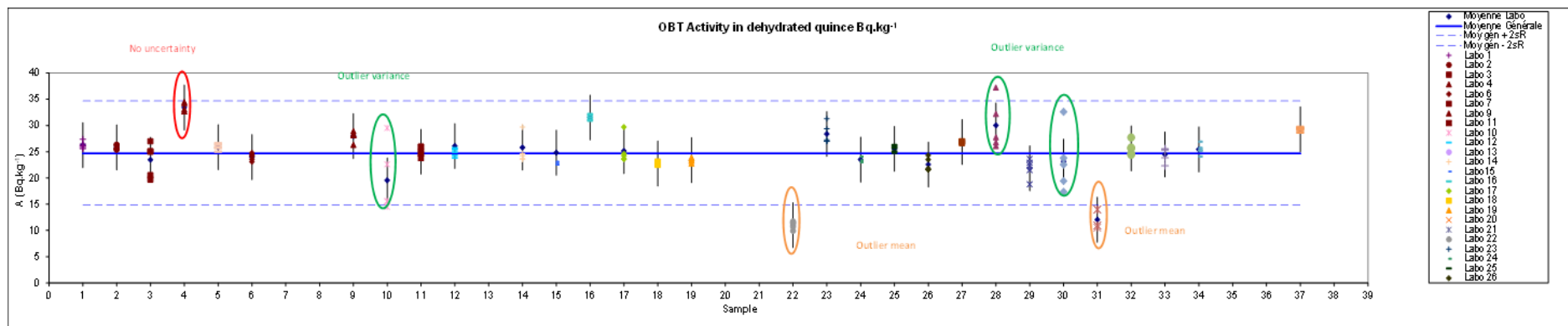
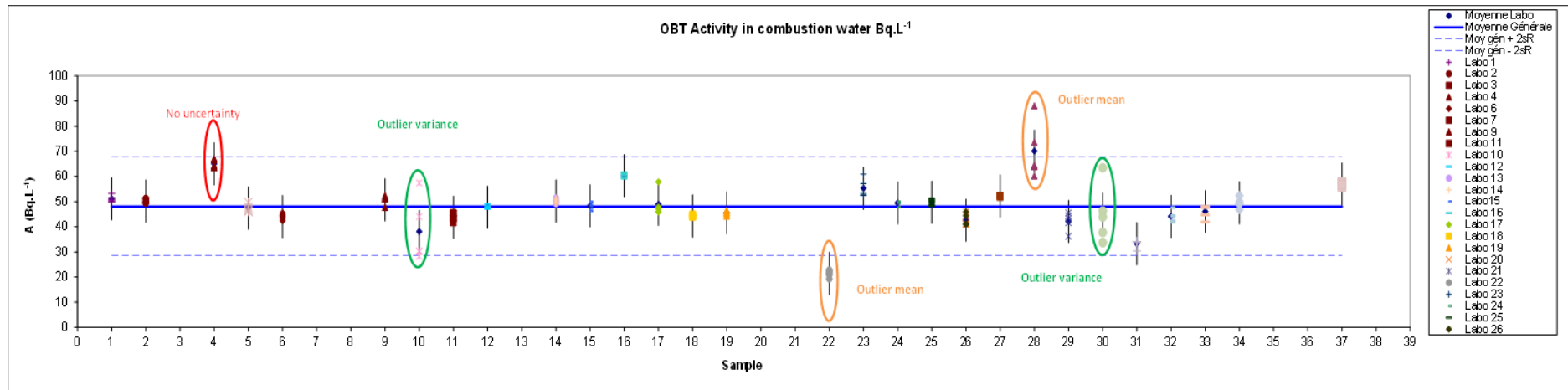
# The 6<sup>th</sup> OBT Intercomparison exercise



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## 6. Evaluation of the results (cont.):

- ANOVA evaluation – by Nicolas Baglan



# The 6<sup>th</sup> OBT Intercomparison exercise

## 6. Evaluation of the results (cont.):

- Assigned values – ANOVA approach

Bq/L

<b>Overall mean</b>	<b>47.6</b>
Variance of repeatability	22.3
Inter lab variance	10.7
Variance of reproducibility	33.0
Repeatability standard deviation ( $s_r$ )	4.7
Reproducibility standard deviation ( $s_R$ )	5.7

Bq/kg

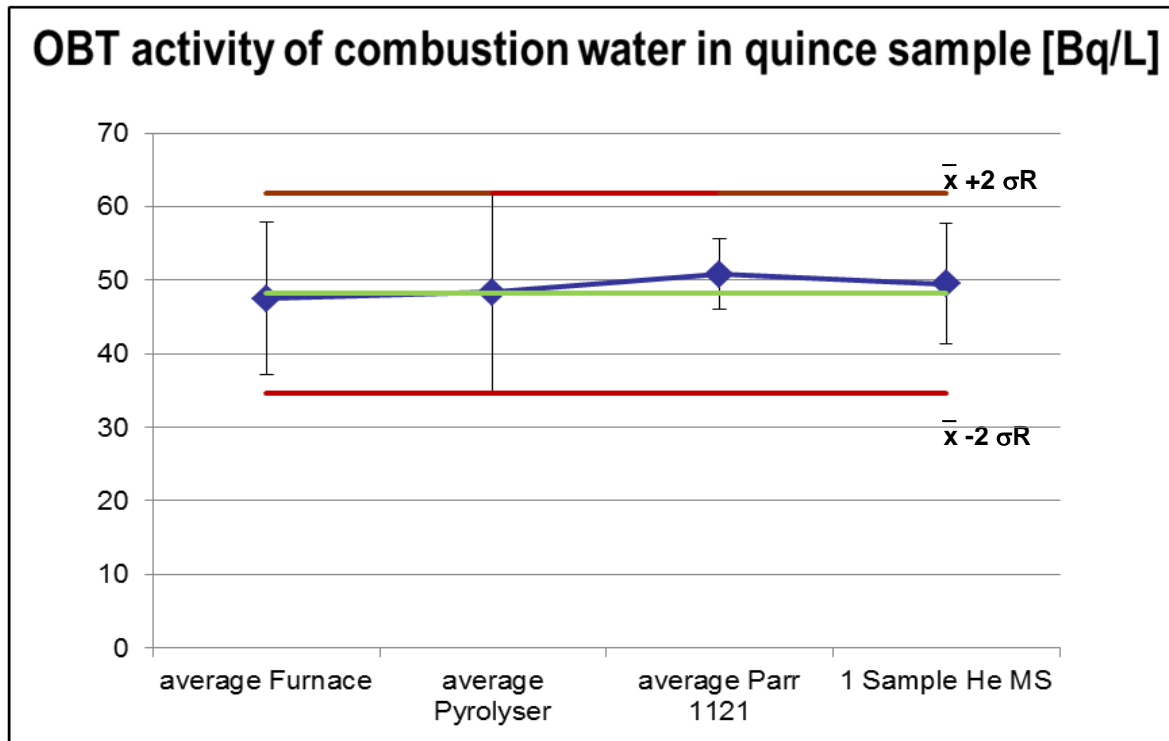
<b>Overall mean</b>	<b>25.2</b>
Variance of repeatability	4.9
Inter lab variance	7.3
Variance of reproducibility	12.2
Repeatability standard deviation ( $s_r$ )	2.2
Reproducibility standard deviation ( $s_R$ )	3.5



# The 6<sup>th</sup> OBT Intercomparison exercise

## 6. Evaluation of the results (cont.):

- OBT average activity by sample treatment:



# The 6<sup>th</sup> OBT Intercomparison exercise



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## 7. Conclusions:

- The results obtained during the exercises are encouraging as an increased number of participating labs didn't change the observed dispersion of the results for a similar activity level. Therefore, the results didn't seem to be dependent on the analytical procedure used.
- The results confirmed that this matrix with low level activity could be used as a reference material. However, some points need to be improved for the next exercises.
- Since the 8<sup>th</sup> OBT Workshop in Constanta, Romania, the scientific committee of the OBT International Group strengthen some remarks to the participants to be taken into consideration for the future OBT intercomparison exercises:
  - 1) five replicates of the activity concentration's determinations should be performed and reported by the participating labs with the corresponding uncertainties to make possible the statistical treatment;
  - 2) the reporting form in the Excel file indeed proved that is very useful and should be used by the participants without any modifications or locking of the sheets or tables and filled with more information about the combustion method, measurement conditions and calculation formula;

# The 6<sup>th</sup> OBT Intercomparison exercise



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## 7. Conclusions:

- 3) the hydrogen percentage value used by the labs should be filled in (experimental value from the literature or the value provided by the organizing lab);
  - 4) the number of participating labs should be limited to 30 and the sample will be delivered on the first register-first served basis and also taking into account if the registered lab provided the results at the previous exercises;
  - 5) there will be an OBT IC exercise and an OBT workshop at every 2 years (one year exercise and the next year workshop) to allow more time for new scientific work to be conducted and presented.
- At the same time, this group could take advantage of this large collaboration to examine the chance to start a program combining analysis and modelling to improve our knowledge of tritium transfer data.
  - Moreover, aiming to provide CRM's in the future, the remaining intercomparison samples could be used to check the stability versus time after storage in the organizing lab for a period of up to 5 years through small inter-laboratory exercises (typically 5 labs).

# Acknowledgements

- All contributing Laboratories to the 6<sup>th</sup> OBT IC exercise
- ICSI, Rm. Valcea – Romania for Hydrogen % determination
- My colleagues from the Environmental Laboratory for their work for the 6<sup>th</sup> OBT intercomparison exercise
- SCK-CEN to host the 9<sup>th</sup> OBTWworkshop.



Always remember:

**Dr. Dan Galeriu** – IFIN-HH, Romania and **Dr. Catherine Cossonnet** – IRSN, France



## THANK YOU !