Improvement and evaluation of the combustion method for organically bound tritium analysis

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Introduction of our Institute and laboratories

About the PhD course of the Graduate School of Health Sciences at Hirosaki University

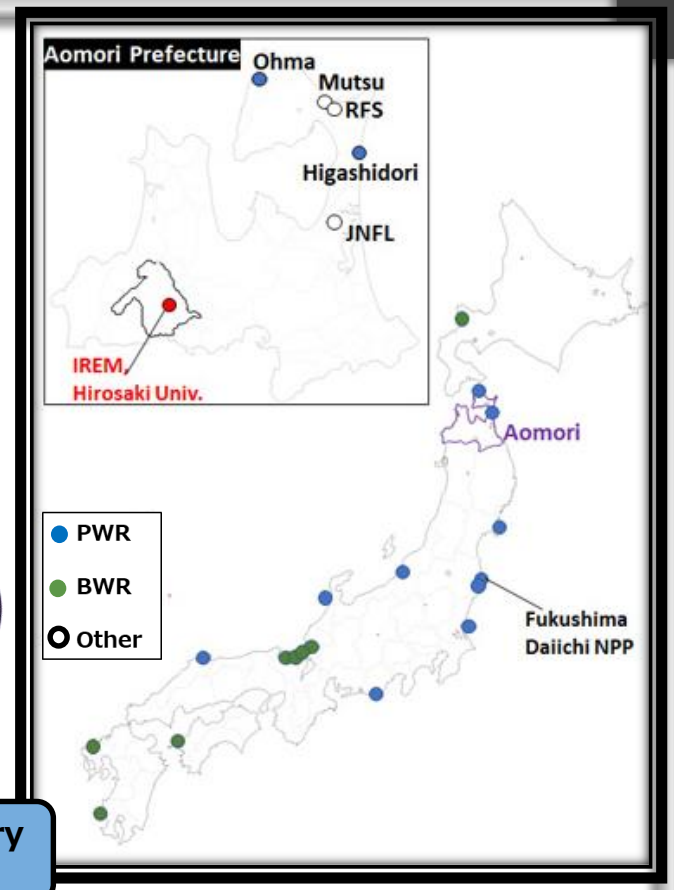
➢Trains highly skilled professionals and leaders in radiation exposure medicine as well as educators and researchers who can contribute to the development of this field of study as people who can prepare for radiation-related emergency exposure accidents.

HIROSAKI UNIVERSITY

About the Institute of Radiation Emergency Medicine (IREM)

➢ The institute was established to help facilitate and health management of radiation exposure at nuclear facilities and medical facilities throughout Japan, and to train professionals who can respond to radiation exposure incidents in emergency situations. In addition to providing educational support in various faculties and graduate schools, the institute is also engaged in activities to further promote basic research on radiation emergency medicine at Hirosaki University.

IREM



Department of Radiation Measurement and Physical Dosimetry

Department of Risk Analysis and Biodosimetry

Department of Radiochemistry and Radioecology

Department of International Cooperation and Collaborative Research

Department of Radiation Emergency Medicine

Prof. Naofumi Akata

➢This division develops new scientific methods for the environmental dynamics of radionuclides and for difficult-to-analyze radionuclides

➢Hirosaki University is the only university in Japan conducting Organically Bound Tritium (OBT) research.

Hirosaki University
IREM HP
https://irem.hirosaki-u.ac.jp/en/

Background

- The Japanese government decided to release Advanced Liquid Processing System (ALPS) treated water containing tritium into the ocean, which is generated by the decommissioning work of the Fukushima Daiichi Nuclear Power Plant in April 2021.

- The spent nuclear fuel reprocessing plant is located in Rokkasho Village, Aomori Prefecture, and tritium is generated through the operation.

- Fusion energy is also expected to be a next-generation source of clean energy in carbon-neutral efforts to achieve a decarbonized society, and the restart of nuclear facilities is also being considered.

  ➢**There is concern about the environmental impact of tritium release.**

  ➢ **It is important to determine the background concentration level of tritium in the environment before any accidental or planned releases of tritium into the environment**

Tritium concentration in the environment and issues

There are many elements of tritium behavior that are still unclear because there is a lack of information on tritium concentrations in the environment, especially in biological samples.

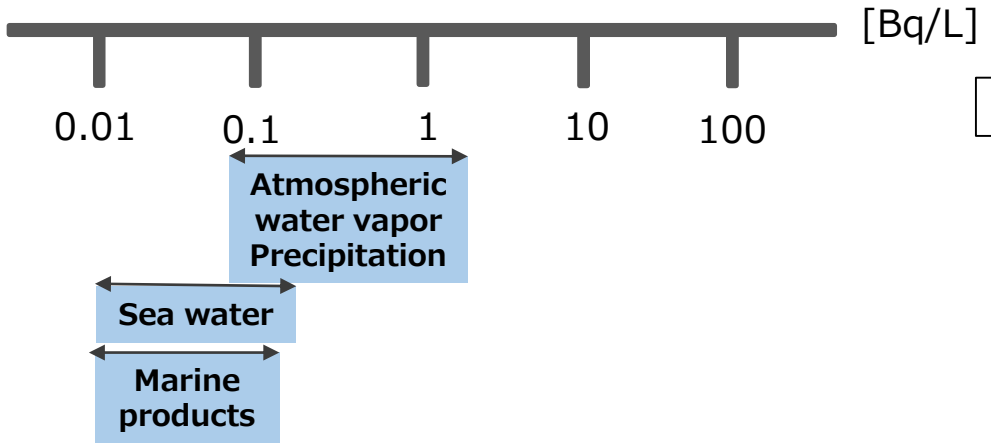


Figure 1 Tritium concentration in the environment

➢High-precision analysis is required due to the low concentration of tritium in the environment.

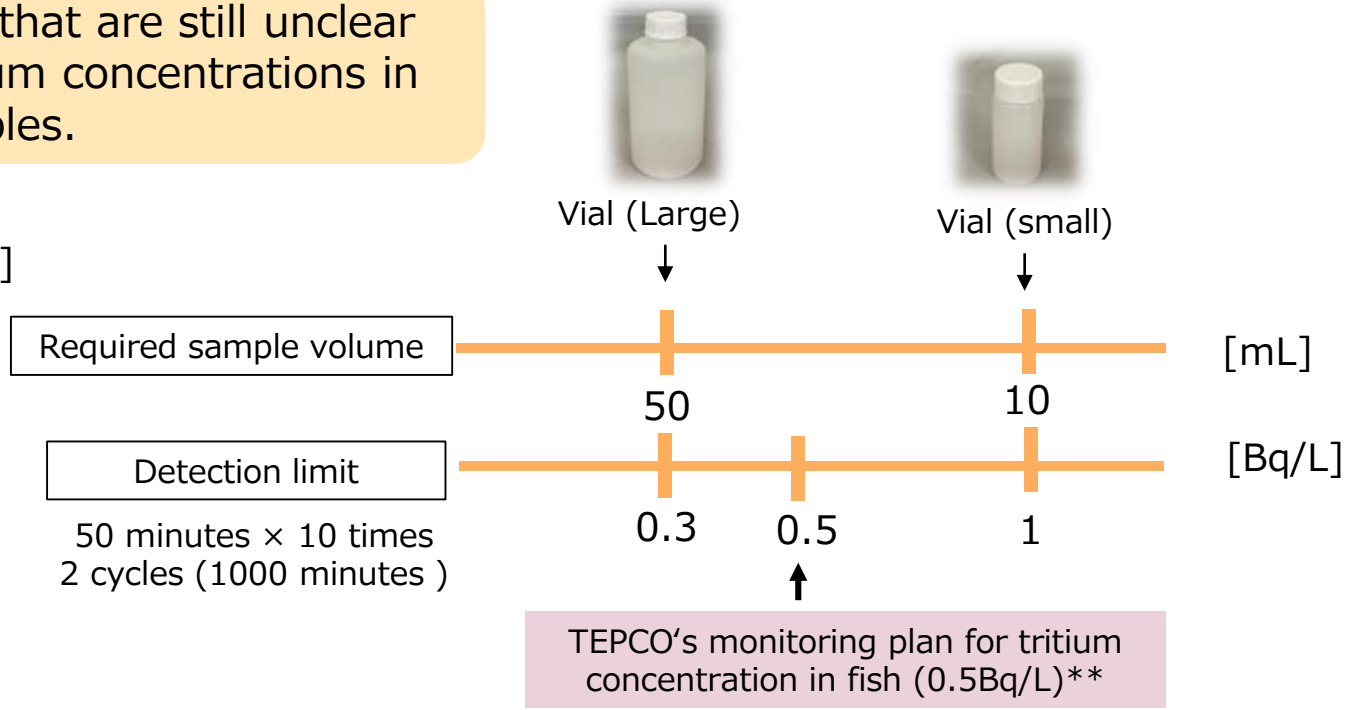


Figure 2 Relationship between sample volume and detection limits in liquid scintillation counters*

➢ Increased sample volume and measurement time are required for highly accurate analysis in order to reduce the detection limit.

*Ministry of Education, Culture, Sports, Science, and Technology radioactivity measurement method Series 9 "Tritium analysis method"
**https://www.tepco.co.jp/decommission/information/implementation/pdf/reference.pdf

Tritium analysis in biological samples

- Takes a long time because several pretreatment processes are required before measuring a single sample.
- Because the combustion speed varies depending on the sample and there is a risk of sample loss and equipment damage due to sudden ignition, the combustion process necessitates the use of skillful techniques in order to burn completely and obtain combustion water.

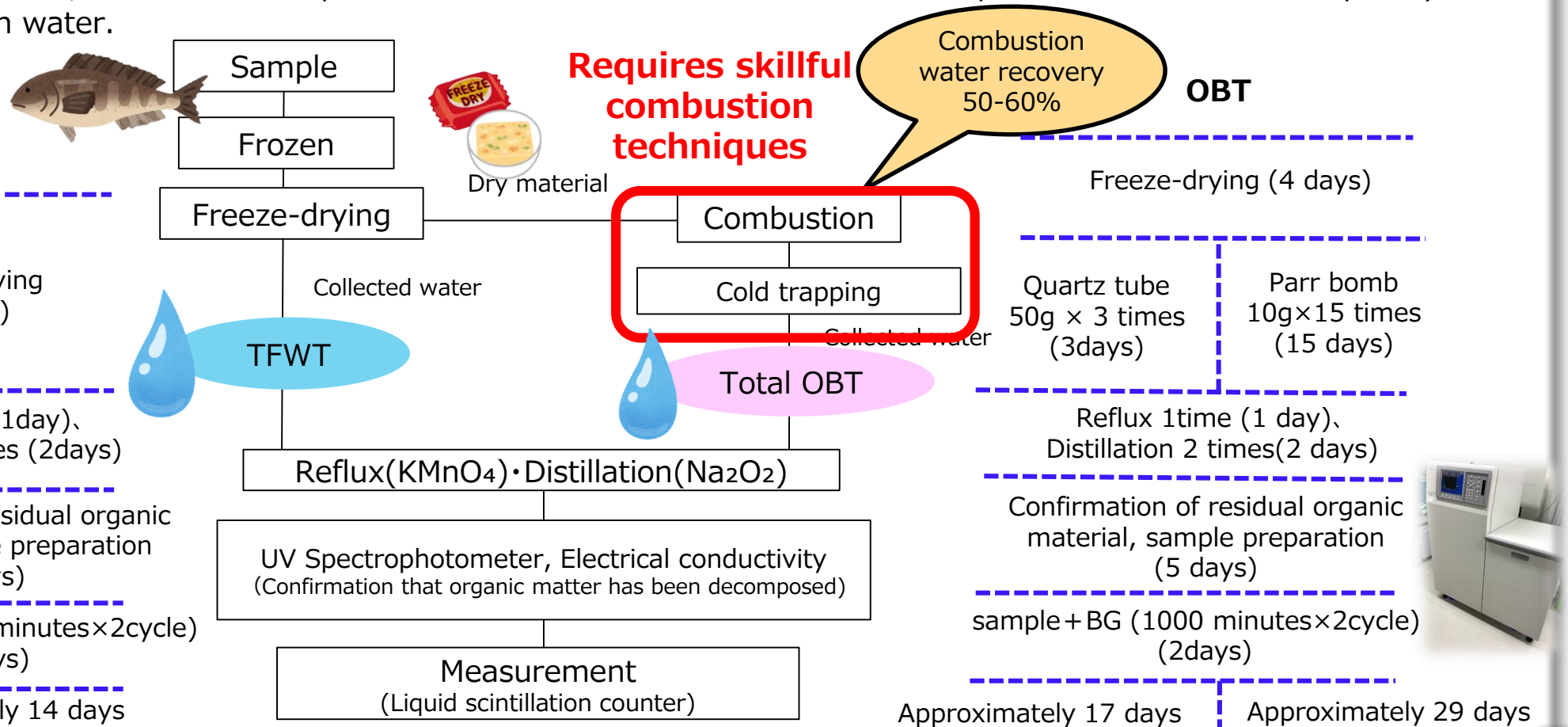


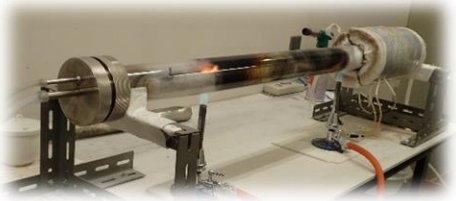
Figure 3 Tritium analysis in biological samples*

* Ministry of Education, Culture, Sports, Science, and Technology radioactivity measurement method Series 9 “Tritium analysis method”

Characteristics of combustion equipment

Table 1 Characteristics of equipment used for combustion testing for OBT analysis

	Advantages	Disadvantages	Combustion water/1 time	Required number of combustions	
				Sample volume 10 mL	Sample volume 50 mL
Quartz tube	・Large amount of sample can be burned at one time (100g)	・**Required for combustion techniques** ・Needed monitor during combustion	50mL	1	1 to 2
Parr bomb (Commercially available)	・Easily combustible ・Combustion time is short (4 hours)	・Limit amount of sample	5 mL	5	**15**
Pyrolyser (Commercially available)	・Automatic combustion	・Limit amount of sample	10mL	3	**7**



Quartz tube

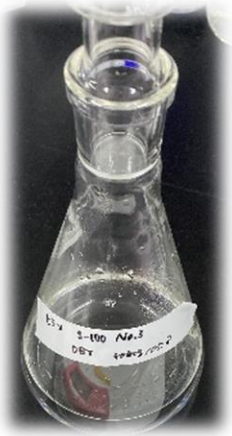
Parr bomb
1121

Raddec : Pyrolyser-6 Trio

Need combustion equipment that can easily, safely, and stably collect as much as possible!

Objective

Development of combustion system for organic materials that can operate with easily and safety, and are capable of efficiently obtaining combustion water

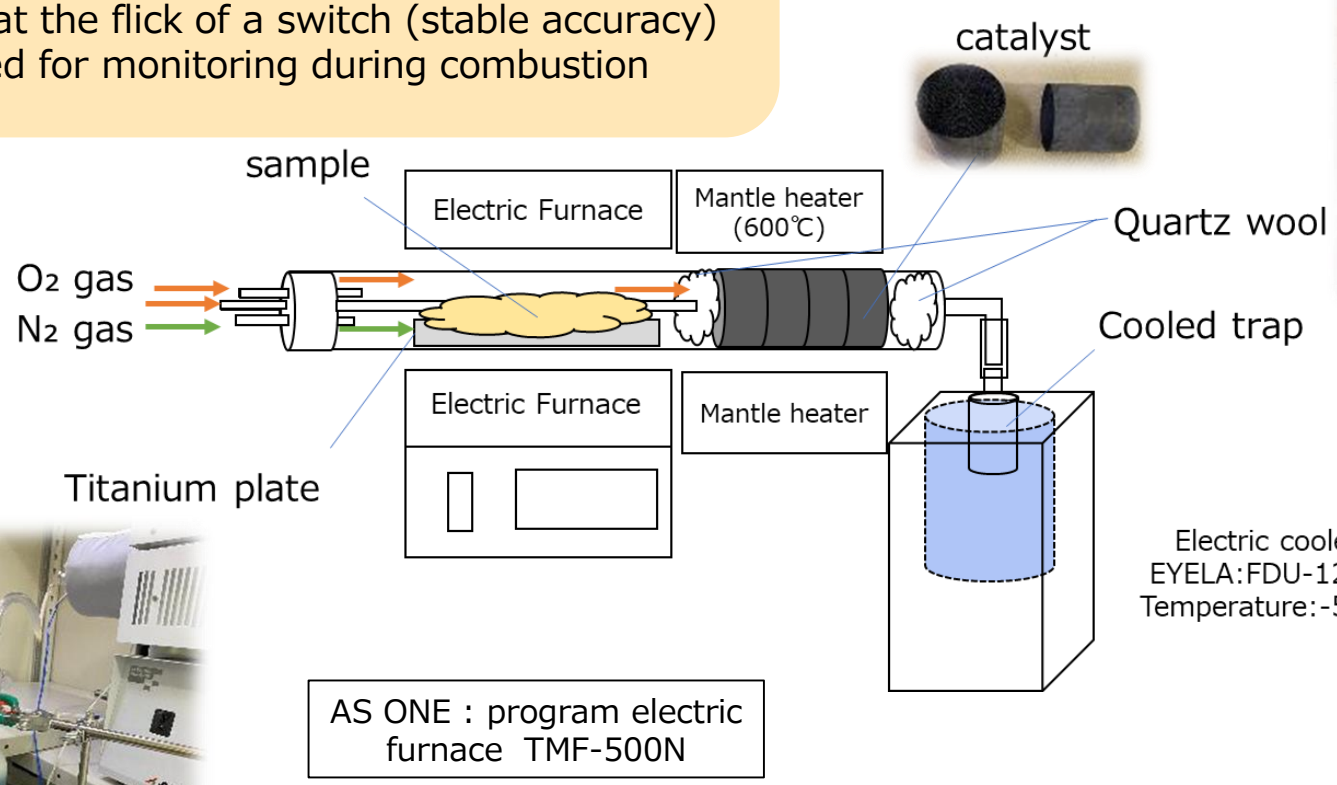


Accumulating OBT monitoring data and advanced environmental and biological effect assessments

Contributing to the safety of residents by assessing the environmental impact of decommissioning works at the Fukushima Daiichi Nuclear Power Plant and correctly assessing the impact of tritium

Semi-automatic combustion system

Advantage
- Can burn 15-40 g sample volume at a time
- Does not cause sudden ignition (safety)
- Burns at the flick of a switch (stable accuracy)
- No need for monitoring during combustion



Electric cooler
EYELA:FDU-1200
Temperature:-50℃

AS ONE : program electric furnace TMF-500N

Figure 4 Semi-automatic combustion system

Combustion conditions

☑Prevents sudden ignition

☑No retention of combustion gas in the quartz tube

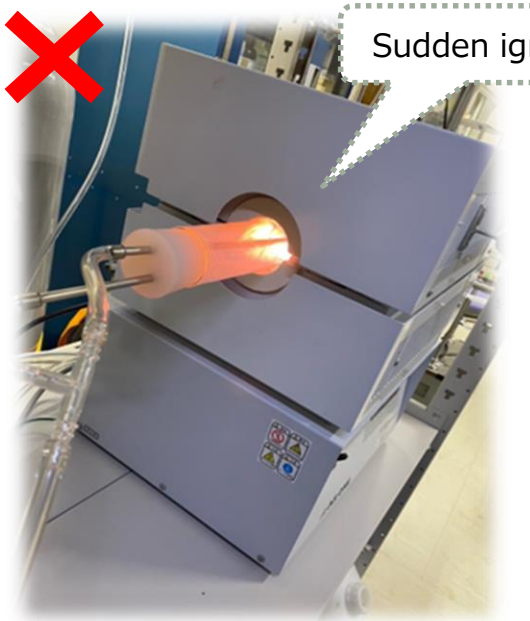
☑Combustion gas is completely oxidized, combustion water is clear and colorless

☑Combustion water recovery rate of 50-60%

☑ No combustion water remains in the quartz tube

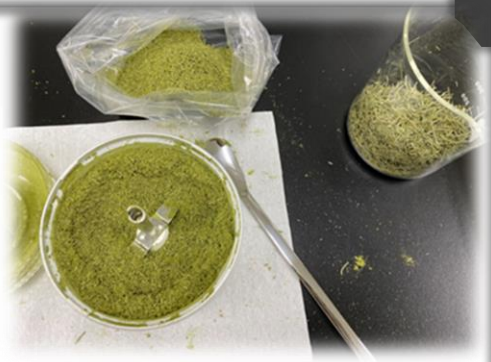
Low combustion recovery rate

Combustion gases are not completely oxidized



Sudden ignition

Experiments



○Combustion test of plant samples by a semi-automatic combustion system

Target materials : apples, pine needles

➢Examination of temperature program and combustion conditions for automatic combustion

➢Examination of sample shape

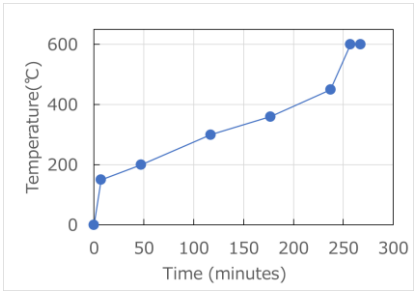
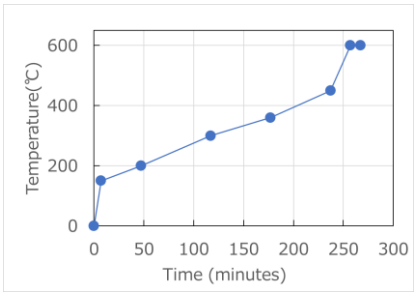
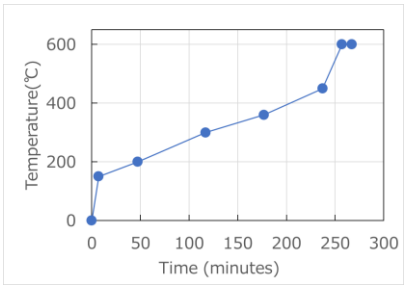
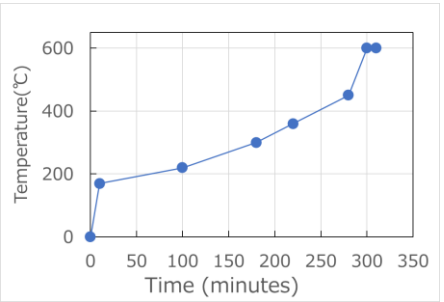
➢Evaluation of combustion water recovery rate

○Combustion tests with standard pine needle samples

➢The validity of the method using this system was verified by comparing the analyzed values of other combustion equipment.

Combustion test of plant sample

Table 2 Combustion test results of plant samples

	Apple	Apple	Pine needle	Pine needle
Before				
After				
Program				
Gas flow	N_2 : 0.20 L/min O_2(sample side) : 0.20 L/min O_2(catalyst side) : 0.10 L/min	N_2 : 0.20 L/min O_2(sample side) : 0.20 L/min O_2(catalyst side) : 0.10 L/min	N_2 : 0.18 L/min O_2(sample side) : 0.20 L/min O_2(catalyst side) : 0.20 L/min	N_2 : 0.30 L/min O_2(sample side) : 0.10 L/min O_2(catalyst side) : 0.30 L/min
Combustion of dry sample amount and combustion water(CW) recovery amount	Block 15.8～21.8 g dry(n=7) **5.5±0.1g CW/10 g dry**	Powder 21.2 g dry(n=1) **5.5 g CW/10 g dry**	Grind 21.2、22.2 g dry(n=2) **5.2g CW/10 g dry** **5.3g CW/10 g dry**	Powder 17.4～33.5 g dry(n=18) **5.1±0.2 g CW/10 g dry**

・Under the created temperature program and combustion conditions, it was possible to continuously collect a certain amount of combustion water without causing sudden ignition.
・Powdered samples and samples containing high oil content require adjustment of sample volume and gas flow rate.
・Optimal sample volume and sample shape for automatic combustion
➢ Apple(Block) : about 20 g ➢Pine needle (Powder) : about 27 g

Evaluation of combustion water recovery rate

Hydrogen content
Hydrogen content was measured using an elemental analyzer (NCS2500, Thermo, Germany)

Plant samples　Apple : 6.57 ± 0.24 %　　Pine needle(literature value*) : 6.51-6.58 %

Calculation of theoretical values

Combustion water (g) = Weight of dried sample(g) × 18/2 × Hydrogen content (%)/100

Table 3 Evaluation of combustion water recovery per 10g dry weight in apple and pine needle samples

	Apple (block)	Apple (powder)	Pine needle (grind)	Pine needle (powder)
Theoretical value (g)	5.9	5.9	5.9	5.9
Measured value (g)	5.5	5.5	5.3	5.1
Combustion water recovery rate (%)	93	93	88	86

The recovery of combustion water in environmental samples is about 80% according to literature values**, and it was confirmed that the recovery of combustion water using this system is good.

* Akata, N et al. J. Radioanal. Nucl. Chem, 319: 1359-1363, 2019.
** Huang, Y.J. et al. J. Environ. Radioact., 134, 2014.

Combustion tests with standard pine needle samples

Standard reference material 1575a, commercially available from the National Institute of Standards and Technology(NIST)

Product of North Carolina(2002)
Species : *Pinus taeda*

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CrossMark

Determination of non-exchangeable organically bound tritium concentration in reference material of pine needles (NIST 1575a)

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Abstract
Non-Exchangeable Organically Bound Tritium (Nx-OBT) in a biological reference material: NIST 1575a Pine Needles was determined by radiometry and noble gas mass spectrometry. Nx-OBT concentration ranged from 1.08 to 1.45 Bq L^{-1}-combustion water (CW) (n = 4) with mean value (± S.D.) of 1.25 ± 0.15 Bq L^{-1}-CW in radiometry and ranged from 1.12 to 1.35 Bq L^{-1}-CW (n = 3) with mean value of 1.22 ± 0.25 Bq L^{-1}-CW in mass spectrometry. For the Pine Needles reference material, there is no proposed value about Nx-OBT, but our results showed a good agreement with the data determined by different methods. Thus, it is useful material for the quality control of Nx-OBT measurements.

Keywords Non-exchangeable Organically Bound Tritium · Reference material · Pine needle

NIST Special Publication 260-156

Certification of NIST Standard Reference Material 1575a Pine Needles and Results of an International Laboratory Comparison

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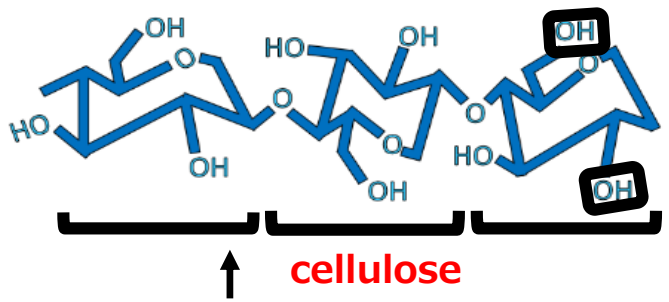
June 2004

Validation of semi-automatic combustion system using standard pine needle samples

Exchangeable OBT (Ex-OBT)
Easily replaced by the surrounding hydrogen
(-OH, -COOH, etc.)



Non-Exchangeable OBT (Nx-OBT)
^{3}H bound to the carbon chain that does not exchange

Pine needle 1575a
(50g×5 bottles)

Repeat three times

Add about 500mL of tritium-free water
24 hours leave to soak
Pre-frozen

Freeze-drying

Dried sample

Add about 500 mL of tritium-free water to about 250 g of dried sample, soak for 24 hours, pre-freeze, and freeze-drying.

Combustion

Combustion water (Nx-OBT)

Reflux・Distillation

Confirmation of residual organic matter
(UV spectrometer)

Measurement of tritium concentration
sample : scintillation cocktail
(Ultima Gold LLT)＝50mL : 50mL

Placement in tritium-free water

Figure 5 The analytical flow of Nx-OBT using standard samples of pine needles

Combustion tests with standard pine needle samples –Result –

Table 4 Results of Nx-OBT concentration from semi-automatic combustion system and quartz tube equipment and mass spectrometry

	This study	Quartz tube* (reported value)	Mass spectrometry* (reported value)
	Nx-OBT concentration Bq/L	Nx-OBT concentration Bq/L	Nx-OBT concentration Bq/L
1	1.5 ± 0.4**	1.4 ± 0.1**	1.2 ± 0.1 ***
2	1.3 ± 0.4	1.3 ± 0.1	1.1 ± 0.1
3	1.8 ± 0.2	1.1 ± 0.1	1.3 ± 0.1
4	1.7 ± 0.2	1.2 ± 0.1	-

Reference date: March 1, 2002
The detection limit (this study 1 & 2) : 0.36 Bq/L measurement time 1000 minutes (Raytech LB5)
The detection limit (this study 3 & 4) : 0.22 Bq/L measurement time 2000 minutes (Raytech-LB7)
*Akata et al. 2019, https://doi.org/10.1007/s10967-018-6397-9
**Counting error
*** Standard deviation

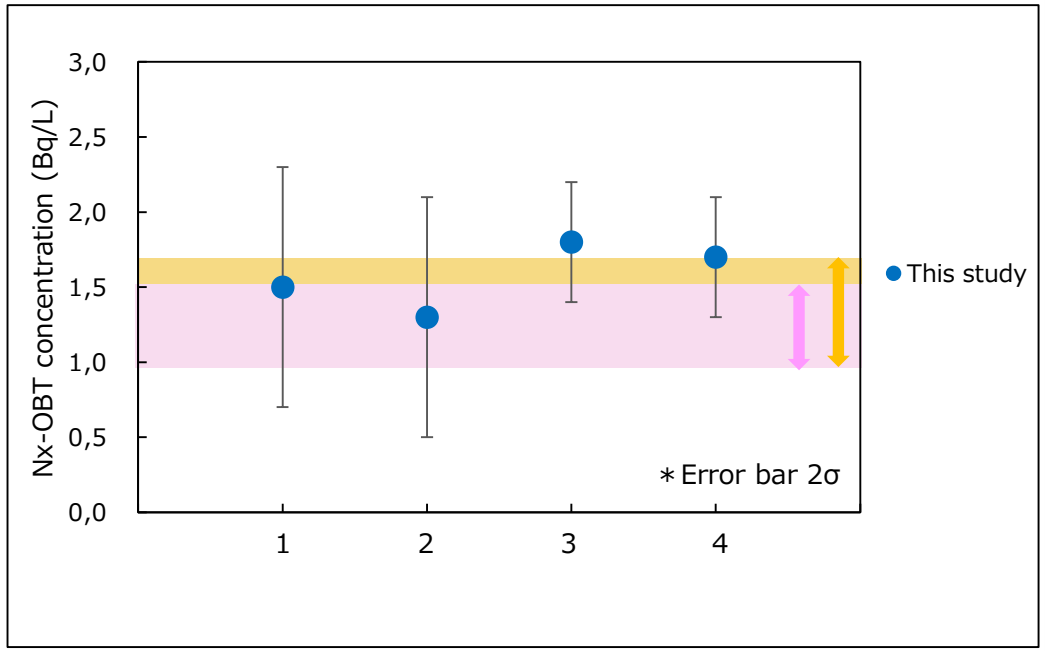


Figure 6 Comparison of the analysis of this study with that of other instruments
: range of Quartz tube
: range of Mass spectrometry
*Measurement 1&2 were 1000 minutes
**Measurement 3&4 were 2000 minutes

The results of this study suggest that the combustion method used is effective in measuring the level of OBT in the samples analyzed. However, it is important to note that the measured values of OBT may be subject to variation, which could be attributed to factors such as the half-life of the OBT present in the samples.

Conclusion

Table 5 Characteristics of each combustion system

	Advantages	Disadvantages	Combustion water/ 1time	Number of times required for combustion	
				Sample volume 10 mL	Sample volume 50 mL
Semi-automatic combustion system	・Easily to combustion ・Prevent ignition	・The amount of sample that can be filled at one time is inferior to quartz tube combustion equipment	**15mL (Plant sample)**	**2**	**5**
Quartz tube	・Large amount of sample can be burned at one time	・Required for combustion techniques ・Needed monitor during combustion	50mL	1	1 to 2
Parr bomb	・Easily to combustion ・Combustion time is short	・Limit amount of sample	5 mL	5	15
Pyrolyser	・Easily to combustion	・Limit amount of sample	10mL	3	7

➢**Combustion systems using program tube furnaces can prevent ignition, safely and automatically burn and easily obtain combustion water by adjusting the temperature program, gas flow rate, sample shape, and sample volume depending on the sample.**

➢**If a combustion test is carried out targeting a lower detection limit of 0.3 Bq/L and combustion is carried out once a day in two systems, it is possible to complete the combustion operation in two days.**

Future Plan

- Identify substances that cause ignition using TG(Thermogravimetry)-DTA(Differential thermal analysis)-FTIR(Fourier transform infrared spectrometer) and elucidate the mechanism of ignition.

- Fish standard samples are analyzed to verify the validity of this combustion system in fish samples.

Related references

- S. Okada and N. Momoshima, Health Phys, 1993
- Ministry of Education, Culture, Sports, Science, and Technology radioactivity measurement method Series 9 “Tritium analysis method”
- Huang, Y.J. et al. J. Environ. Radioact., 134, 2014.
- Akata, N et al. J. Radioanal. Nucl. Chem, 319: 1359-1363, 2019.
- Tamari, T et al. Jpn.J. Health Phys., 55(3)、136-143, 2020. (in Japanese)
- Tamari, T et al., Fusion Sci. Technol., 60, 1252-1255, 2011.
- Akata, N et al. Plasma and Fusion Research, 11, 2405017, 2016.
- TEPCO HP: https://www.tepco.co.jp/decommission/information/implementation/pdf/reference.pdf

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Thank you for your kind attention