A New Pretreatment Technique for Environmental Tritium Analysis with Microwave Heating Method*)

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The conventional method for FWT and OBT analysis is a liquid scintillation counting method after freeze-drying and combustion of the sample. However, pretreatment for FWT and OBT analysis are complicated and time consuming processes over weeks. Thus, we propose the application of microwave heating technique to save time and effort of the pretreatment of plant samples for FWT analysis. To understand the behavior of the combustion and drying of organic samples, we conducted TG/DTA analysis of pine needle samples. It is found that the sample has to be heated up to 100 - 110 °C for complete drying under N_2 gas flow condition. Then, we tried the water recovery from fresh pine needle samples by the multi-mode microwave heating system. As a results, it was provided to good recovery yield achieved more than 97% under these experimental conditions. This result shows more preferable for the pretreatment of organic samples by microwave irradiation method than the conventional method.

Keywords: Tritium analysis, FWT, OBT, microwave, pretreatment

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1. Introduction

Tritium (^{3}H) is a radioisotope of hydrogen and it decays to Helium-3 with a half-life of 12.3 y. Most of natural tritium is produced by nuclear reaction of nitrogen and oxygen atoms with cosmic rays in the stratosphere. Nuclear weapons testing in the atmosphere released large amounts of anthropogenic tritium into the environment. Nuclear facilities are also releasing tritium into the environment [1]. In the future, nuclear fusion reactors will have a large inventory of tritium as fuel [2]. Although tritium as fuel is burned in the core plasma and contained in the facility, small amounts of tritium will be released as gaseous exhaust and drain water into the environment.

The deuterium plasma experiment is being planned to produce higher performance plasma using the Large Helical Device (LHD) of the National Institute for Fusion Science (NIFS) [3]. In the experiments, a small amount of tritium will be produced by the D(d, p)T reaction in D plasma. Therefore, it is important to understand the tritium concentration in environmental samples for radiation safety and environmental impact assessment [4]. Tritium in environmental organic samples usually consists of free water tritium (FWT) and organically bound tritium (OBT). The FWT exists as HTO form, and its behavior is similar to natural water. On the other hand, OBT is tritium bounded to organic molecules (or carbon). The OBT has a longer biological half-life and higher incorporation to organic materials than the FWT [5]. The conventional method for FWT and OBT analysis is a liquid scintillation counting method after freeze-drying and combustion of the sample as summarized in MEXT report [6]. However, pretreatment operation for FWT and OBT analysis are complicated and time consuming processes over weeks. Therefore, it is necessary to develop the simple and quick technique.

It is well known that microwave irradiation technique is useful and convenient. Microwave irradiation to materials is a new comer for our civilization with a history of only half century. The microwave heating has the dielectric loss, magnetic loss, joule heating, and so on with respects to the kind of materials, for example with the dielectric materials, magnetic materials, metal powder, and so on. It clearly suggests that the energy transfer mechanism in microwave heating is quite different from the traditional heating process. In particular, microwave heating has the characteristic of volumetric heating in materials.

Thus, we propose the application of microwave heating technique to save time and effort of the pretreatment of

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plant samples for FWT analysis. In this paper, we report the preliminary result of endothermic and exothermic phenomena by using thermal analysis instrument and multimode microwave drying.

2. Materials and Method

2.1 Samples

Fresh one-year-old pine needle samples were collected at our institute (35°19'N, 137°10'E) in June 2014. Collected samples were sealed in water-vapor-tight laminate bag (AL-30L, Seisannipponsha, Japan) and was kept in a refrigerator.

2.2 Thermal analysis

Thermal analysis is useful tool to evaluating the endothermic phenomena, exothermic phenomena and weight change characteristics. Thermogravimetric Analysis (TG) observes the weight change in a sample with respect to the temperature. Negative weight change means desorption of volatile components from the sample, and positive weight change means absorption of gaseous components from the surrounding atmosphere. On the other hands, Differential Thermal Analysis (DTA) observes the temperature of sample as compared to the reference material. Positive and negative peaks mean exothermic change and endothermic change, respectively. In this study, TG/DTA analysis was done [7]. A few collected fresh pine needle samples were cut into fragments with a few millimeter long. The cut samples of approximately 30 mg was placed into Pt cup (ϕ: 5 mm), and the TG and DTA of samples were measured by using TG/DTA analyzer (EXSTAR6000, Seiko Instrument, Japan). The experimental conditions are as follows.
Atmosphere: N_2 flow (100 cc min^{-1}).
Heating rate: 5 °C min^{-1} up to 150 °C, 350 °C and 600 °C.

2.3 Microwave heating method

The multimode test furnace, as shown in Fig. 1, was used for this present study [8]. This test furnace with a volume of 0.92 m^3 is equipped with five magnetrons. The magnetron generate 2.5 kW at 2.455 ± 0.030 GHz. Each magnetron has small differences in frequency and the beat of waves occurring in the chamber. In addition, two mode stirrers scatter the standing wave, easing the non-uniformity due to the standing wave.

The fresh pine needle sample (approximately 80 g) with silica wool (both side of sample) was placed in a quartz tube (50 mm ϕ, 500 mm in length). The silicone rubber stopper with tygon tube was provided at each end of tube. We have installed this sample tube in test furnace. The setup of sample tube shown in Fig. 2. N_2 gas (2 L min^{-1}) was supplied to front side of quartz tube through the tygon tube during the microwave irradiation. The tygon tube connected rear position of quartz tube issued out of the test furnace from the small port, glass trap cooled with liquid nitrogen and/or mixture of ice and salt connected for FWT collection. And we measured absorption spectrum in UV range using single-beam ultraviolet visible light spectrophotometer (ASUV-3100PC, Japan) to confirm the situation of recovered FWT (mixing of impurities).

Fig. 1 Test furnace of 2.45 GHz magnetron system.

Fig. 2 Setup of quartz tube with pine needle samples in test furnace.

3. Results and Discussion

Figure 3 show the TG/DTA curve of fresh pine needle samples. Decreasing of TG curve was initiated around 50 °C and terminated at 100 - 110 °C, and it was almost flat from 110 to 250 °C. In DTA curve, a negative peak was recognized at around 100 °C which is endothermic change. And, it was flat curve after 120 °C. These phenomena are typical trend of the dehydration reaction from the samples. This results indicated that dehydration reaction happened by heating, and was completed at 120 °C. After that, TG curve was gradually decreasing from 250 to 400 °C. Then, DTA curve is almost flat. The decreasing trend of TG curve

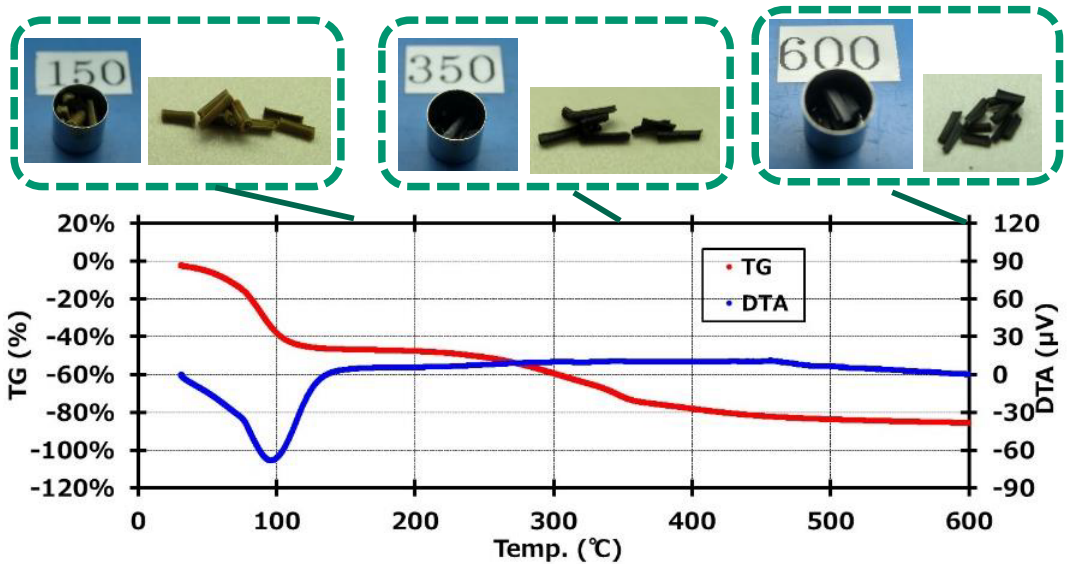

Fig. 3 TG/DTA curve of pine needle samples with photo in the each temperature condition of samples.

Table 1 Summary of condition and results of microwave heating experiment.

	Experiment-1	Experiment-2	Experiment-3
Microwave (kw)	0.5	1.0	2.5
Flow gas	N_2 2L min^{-1}	N_2 2L min^{-1}	N_2 2L min^{-1}
Cold trap	mixture of ice and salt	Liquid nitrogen	Liquid nitrogen
Time (min)	60	30	20
Recovery (%)	93	97	83

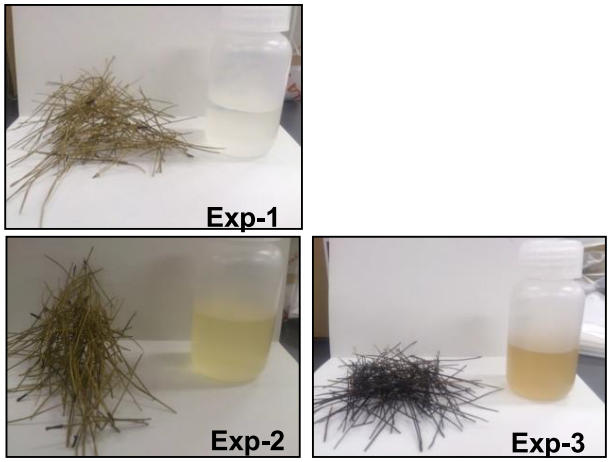

Fig. 4 Sample and recovered water condition after microwave experiment.

means desorption of volatile components from the sample. It is difficult to get oxidation reaction under the N_2 gas flow condition. The heated pine needle samples of 350 °C is not more green color than that of 150 °C. It seems that negative weight change from 250 to 400 °C is desorption of volatile components from the sample. Afterwards, we did not find the clear trend to 600 °C.

Based on TG/DTA analysis, we carried out the microwave heating experiments using big size multimode test furnace. We have conducted three experiments in which microwave outputs are 0.5, 1.0 and 2.5 kw. Experiment time was decided by microwave output power. After microwave heating experiments, the dried pine needle samples were re-dried by oven dryer for calculating the recovery yield of FWT. Summary of experimental conditions and its results are shown in Table 1. Recovery yield of experiment-1, 2 and 3 are 93%, 97% and 83%, respectively. Experiment-3 was worst recovery yield in which the microwave output power was highest. In experiment-3, FWT as water vapor was suddenly flowing from the tube to the cold trap and the rear position of cold trap became hot by heated water vapor. This results indicated that one step liquid nitrogen cold trap system could not collect all water vapor. The color condition of the dried pine needle samples and the recovered FWT water were shown in Fig. 4. The sample color of Experiment-1was similar to 150 °C heated pine needle color of TG/DTA analysis. The color of recovered water was almost transparent. On the other hands, the sample color of Experiment-3 was black as if carbonized at high temperature. The recovered water was brown. These results suggested that experimental condition of Experiment-1 and Experiment-2 were better than Experiment-3. Next, we measured absorption spectrum in UV range of recovered water to confirm the water quality (organic content in recovered water). The results of absorption spectrum were shown in Fig. 5. We confirmed the absorption peak in UV range (vicinity 300 nm)

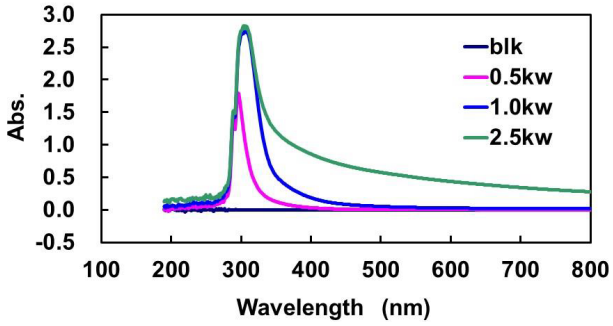

Fig. 5 Absorption spectrum of recovered water (FWT).

at each of the experimental conditions. It is well known that UV-Vis absorption for pure water is hardly observed at 250 nm or more. Therefore, the absorption of more than 250 nm are based on organic materials. The content of organic matter in FWT was depend on microwave output power. This results indicated that the pine needle tissue had been destroyed by microwave energy, and desorbed volatile components has been collected by liquid nitrogen cold trap with FWT (water vapor). The recovered water was purified by atmospheric distillation with addition of $KMnO_4$. There were no marked absorption peak in UV range (250 - 300 nm) by single or double operation. We were required about 4 hours for single distillation operation. The microwave irradiation method for FWT recovery was preferable for saving the pretreatment time. Next step, we have plan to design the FWT recovery system from plant samples using microwave irradiation technique.

4. Summary

We conducted TG/DTA analysis of pine needle samples to evaluating the endothermic phenomena, exothermic phenomena and weight change characteristics. It is found that the sample has to be heated up to 100 - 110 °C for complete drying under N_2 gas flow condition. Next, we tried the water recovery from fresh pine needle samples by the multi-mode microwave test furnace. The recovery yield achieved more than 97% under these experimental conditions (microwave output: 1.0 kw, time: 30 min, N_2 flow: 2 L min^{-1}). This results indicated that sample drying and water recovering technique using microwave irradiation is useful to save the time than the conventional method. We will try to design the microwave irradiation system for FWT recovery from the plant samples based on these preliminary results.

Acknowledgments

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