

#### 4-4 Task 2-1(I) DESIGN AND CONSTRUCTION OF THERMAL DESORPTION MEASUREMENT SYSTEM FOR TRITIUM CONTAINED MATERIALS

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*The dual-mode thermal desorption analysis system was designed and built in Idaho National Laboratory (INL) to examine the evolution of the hydrogen isotope gas from materials. The system is equipped with a mass spectrometer for stable hydrogen isotopes and an ionization chamber for tritium components. The performance of the system built was tested with using tritium contained materials. The evolution of tritiated gas species from contaminated materials was measured successfully by using the system.*

## I. INTRODUCTION

Hydrogen isotope atoms penetrating from plasma into plasma-facing materials (PFMs) are captured by the trap sites in the materials. The physicochemical properties of the trap sites play important roles for the thermodynamics and kinetics of the interactions between hydrogen isotopes and PFMs [1-6].

The trapping energy of hydrogen atom in materials is evaluated by the various methods. The thermal desorption measurement is one of valuable techniques for the evaluation of the trapping energy, the activation energy of hydrogen desorption and the amount of hydrogen atoms trapped. In the thermal desorption measurement, the gaseous hydrogen species evolved from the sample is commonly measured by a mass spectrometer. The thermal desorption spectra from samples containing hydrogen and deuterium gives the information of the isotope effects in hydrogen-trap interactions. The thermal desorption measurements of PFMs are used by many researchers [3-6]. However, a measurement of tritium with a mass spectrometer is difficult because of impairment of a multiplier by  $\beta$ -rays from tritium [7]. Handling of large radioactivity is necessary due to high specific activity of tritium. For these reasons, tritium is commonly measured with higher sensitivity using an ionization chamber, a proportional counter and a liquid scintillation counter.

A thermal desorption measurement system equipped with a mass spectrometer and an ionization chamber (or a

proportional counter) is suitable to measure the evolution of tritium-containing hydrogen isotope gases from the materials. A mass spectrometer works in vacuum conditions, whereas an ionization chamber requires the working gas. In other words, an ionization chamber cannot work in vacuum conditions. Therefore, the measurement system needs to be newly designed for simultaneous measurement of the hydrogen isotope gases containing tritium.

In Japan-US joint research project TITAN, the measurement system equipped with a mass spectrometer and an ionization chamber was designed and constructed in Safety and Tritium Applied Research (STAR) facility of Idaho National Laboratory (INL). The designed system was denoted the dual-mode thermal desorption analysis system (hereafter DM-TDS). The performance of DM-TDS was evaluated by the thermal desorption spectrum of the stainless steel containing tritium. This subsection describes the technical side of DM-TDS in detail.

## II. CONCEPT OF THE DUAL-MODE THERMAL DESORPTION ANALYSIS SYSTEM

DM-TDS was designed to measure the hydrogen isotopes evolved from the materials. The system should detect the main stable hydrogen isotopes by a mass spectrometer and tritium in a trace amount by an ionization chamber. Since ionization chambers require a working gas to obtain ionization current, a gas-flow system should be installed in DM-TDS. The system consists of a mass flow controller, an infrared furnace, a mass spectrometer, an ionization chamber and water bubblers as shown in Fig. 1. Argon gas is selected as the carrier gas.

The sample is placed on the sample stage made from the molybdenum sheet. The thickness and purity of the molybdenum sheet are 0.005 inch and 99.97%, respectively. To make the stage, the sheet was folded by the pliers as shown in Figs. 2 and 3. The stage is directly fixed to the thermocouple (1/8 inch sheath thermocouple with unground junction) and inserted into the quartz tube.

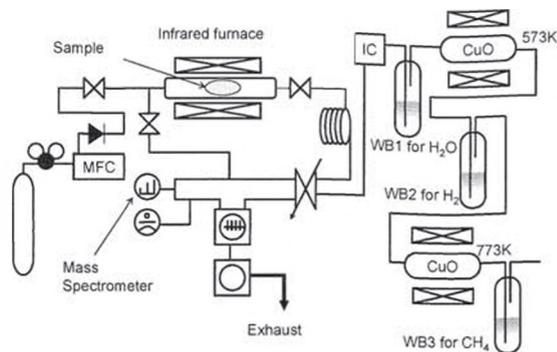


Fig. 1. Schematic diagram of dual-mode thermal desorption analysis system constructed. MFC and IC mean a mass flow controller and an ionization chamber, respectively. WB1 to 3 are water bubblers.

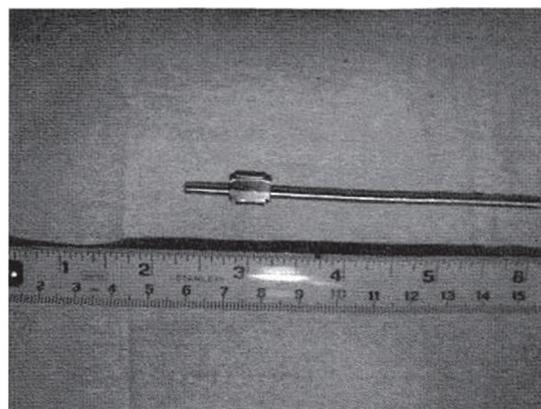


Fig. 3. Photograph of sample stage. The size of stage is around 10 mm × 8 mm. The sheath thermocouple is inserted into the opening of the stage.

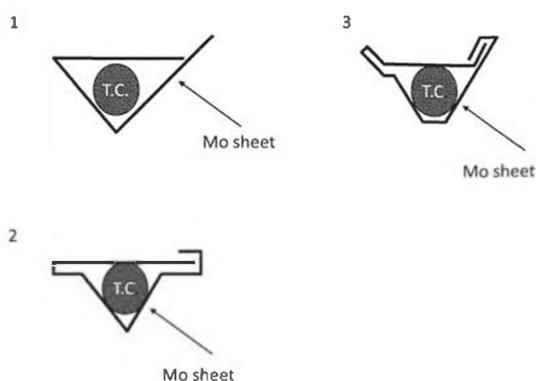


Fig. 2. Preparation of sample stage. The stage is made from a molybdenum sheet. T.C. means the sheath thermocouple.

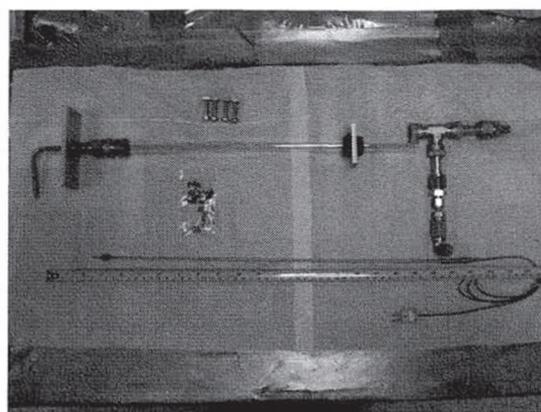


Fig. 4. Photograph of sample stage and unions for quartz tube fixing.

The sample on the stage is heated under argon gas flow by an infrared furnace. The quartz tube is connected by Ultra-Torr connections, because the quartz tube will be contaminated by the tritium evolved from samples and need to be replaced easily. The photograph of the sample holder and the unions for the quartz tube fixing is shown in Fig. 4.

The hydrogen isotope gases evolved from the sample are transported by the carrier gas. A portion of the gas evolved is introduced into the mass spectrometer through the leak valve. A single port leak valve is suitable for a vacuum thermal desorption measurement system but not for a gas-flow thermal desorption measurement system. Since a gas flow can be stuck in a single port leak

valve, real-time measurement of the change in the gas composition is difficult. Hence, we needed to modify the port of the leak valve to be used in DM-TDS. Fig. 5 shows the schematic diagram of the modified leak valve. The modified leak valve is hereafter denoted the dual-port leak valve. The dual-port leak valve is designed to reduce the stuck time of flowing gas. The 1/8 inch tube is inserted into the inside of the single port leak valve through the 1/4 inch bored through type T-shape connection. Since the dual-port leak valve has the inlet and the outlet ports, the carrier gas readily passes through the inner volume of the valve. Fig. 6 shows the dual-port leak valve installed in DM-TDS.

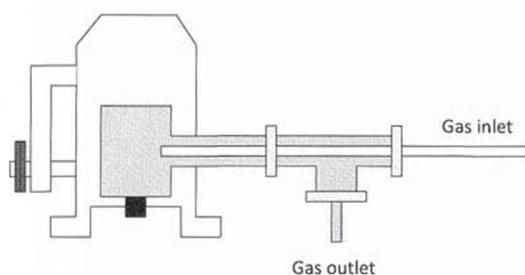


Fig. 5. Schematic diagram of dual-port leak valve.

Three water bubblers connected in series via two CuO beds were installed into DM-TDS as shown in Fig. 1 to determine the amount of released tritium. The first water bubbler captures HTO from the carrier gas. Subsequently, the gas passes through the CuO bed maintained at 573 K to convert HT to HTO, and the second water bubbler captures HTO. The second CuO bed maintained at 773 K oxidizes residual tritiated hydrocarbons into HTO being captured by the third water bubbler. The tritium concentrations in water in the bubblers were determined by a liquid scintillation counting to evaluate the tritium retention in the sample.

Since the ionization chamber is usually calibrated for air, the concentration of tritium in the flowing gas was evaluated from the ionization current by taking account of difference in the W value [8] between argon and air.

The mass spectrometer is evacuated by a turbomolecular pump backed with an oil-sealed rotary pump. The pressure of residual gases was less than  $10^{-7}$  Torr.

### III. PERFORMANCE TEST OF THE DUAL-MODE THERMAL DESORPTION ANALYSIS SYSTEM

DM-TDS was built at STAR facility, INL. The 200 cm<sup>3</sup> ionization chamber was used for the test to detect tritium components. On the other hand, the water bubblers and the CuO beds were not installed in the test. The argon flow rate was set to 26 sccm by the calibrated mass flow controller. Two samples containing tritium were obtained from 1/4 inch stainless steel tubes used in Tritium Plasma Experiment (TPE). The length of sample 1 and 2 were 5 mm and 15 mm, respectively. The carrier gas was fed into the mass spectrometer up to around  $10^{-6}$  Torr via the dual-port leak valve.

### IV. RESULTS AND DISCUSSION

The thermal desorption spectra are shown in Fig. 7. The samples were 1/4 inch stainless steel pipes used in

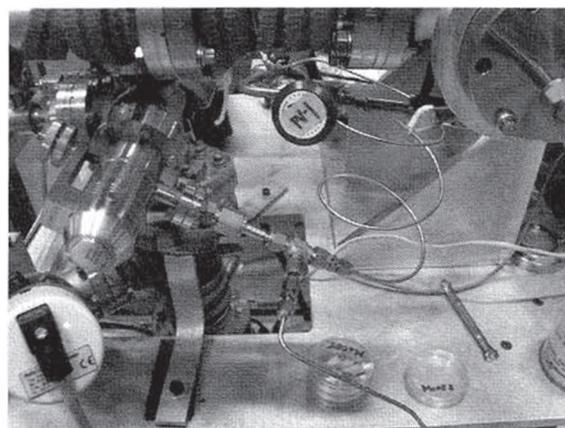


Fig. 6. Photograph of dual-port leak valve installed into DM-TDS.

TPE and consequently contaminated with tritium. In Fig. 7, the abscissa gives the time and the ordinate gives the temperature, the ionization chamber output and the ion current of mass 18 (H<sub>2</sub>O), respectively. The thin line indicates temperature. The black dot means the ion current of mass 18. The bold line is the ionization chamber output. The signal of mass 18 contained much noise, because the mass spectrometer was used before the baking treatment. However, the signal of mass 18 gave the water evolution behavior from the sample with heating. The intensity of mass 18 for sample 1 (5 mm length) increased with increasing temperature and the signal of mass 18 formed a peak at 1150 s. On the other hand, the ionization chamber output formed a peak at 1900 s. This difference was ascribed to the volume of ionization chamber. The relatively large volume causes the resident time of the carrier gas extended in the ionization chamber. In this case, the resident time of the carrier gas in the ionization chamber was calculated to be about 10 min. This result indicates that the relationship between the volume of the ionization chamber and the flow rate is one of the important issues to improve thermal desorption spectra obtained. The intensity of mass 18 increased again when the temperature descended. Subsequently the ionization chamber output also increased.

The intensity of mass 18 and ionization chamber output showed also two peaks for sample 2. We could not have clear explanation for the second peak.

The dual-mode thermal desorption analysis system could simultaneously detect the evolution of the H<sub>2</sub>O vapor and the tritium components. Such capability should

be used for understanding the physicochemical properties

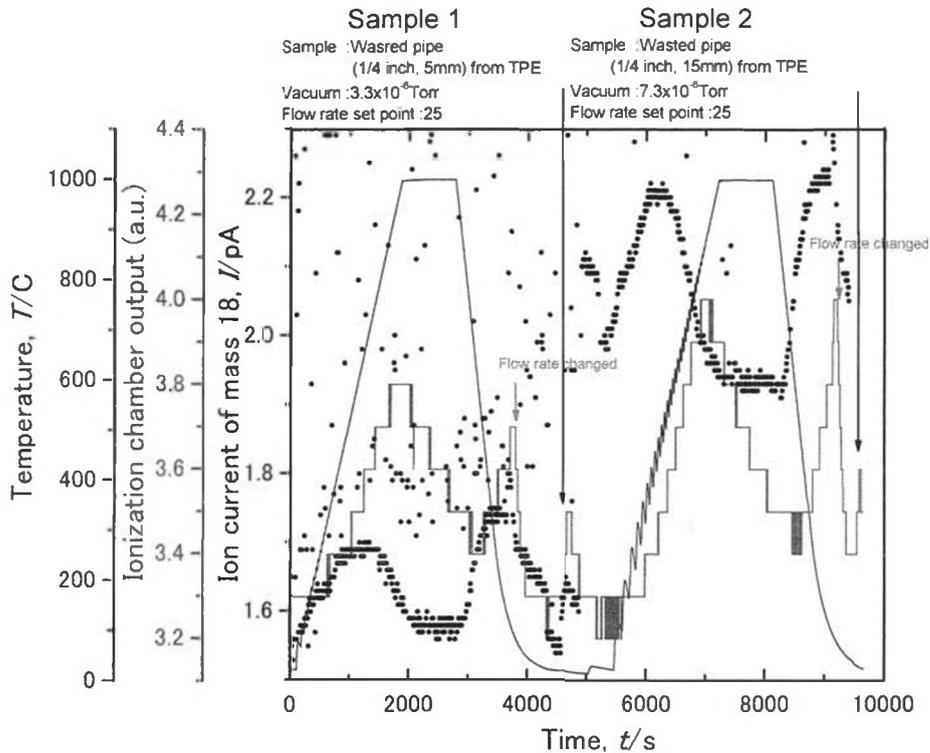


Fig. 7. Thermal desorption spectra for the stainless steel tube containing tritium. The samples were taken from the pipe wastes from TPE. The dots mean the ion current of mass 18 of the mass spectrometer. The bold line is the ionization chamber output.

of the trap sites.

## V. CONCLUSIONS

To understand the physicochemical properties of the hydrogen trap sites, the dual-mode thermal desorption analysis system was designed and built in INL. Using this system, the evolution behavior of the stable hydrogen isotope gases and tritium components can be simultaneously measured. Therefore, the system will give various information on hydrogen isotope retention and release of plasma-facing materials.

## ACKNOWLEDGMENTS

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