Development of Rapid Sampling System of Atmospheric Water Vapor for Tritium Measurement[*)]

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We have developed a rapid sampling system for measuring the tritium in atmospheric water vapor. The system consists of a high-efficiency particulate air filter cartridge, an oil-free compressor, a water-vapor-separating module with hollow fiber membranes, two cold traps, and an oil-free rotary pump. Compressed air (0.4 - 0.7 MPa) is introduced into the water-vapor-separation module, which consists of a stainless steel column containing polyimide membrane tubes. Water vapor permeates through the tubes and is collected by cold traps cooled with dry ice and ethanol. The module is heated with a flexible heater to control its temperature. We have determined the recovery yields under various sampling conditions and find that this system can collect atmospheric water vapor with a recovery yield of > 99 %. This system can thus be a useful tool for understanding short-term observations of tritium in atmospheric water vapor.

1. Introduction

Tritium (^{3}H) is a radioisotope of hydrogen that decays to helium-3 with a half-life of 12.3 y [1]. Many researchers have investigated the sources of tritium in the environment [1–4]. Tritium of natural origin is produced by nuclear reactions between cosmic rays and nitrogen and oxygen atoms in the upper atmosphere. The production rate from this source has been determined to be approximately 0.2 ± 0.5 atoms cm^{-2} s^{-1} (72 PBq y^{-1}), and the global inventory is estimated to be approximately 3.0 kg (1.1×10^{18} Bq). Nuclear weapons testing in the atmosphere also released significant amounts of tritium into the environment before 1963. Although the environmental concentration of this anthropogenic tritium increased rapidly [5], the tritium concentration in environmental samples has now almost returned to natural levels [4, 6, 7]. Nuclear facilities also release tritium into the environment [1, 2]. In addition, nuclear fusion reactors will require a large inventory of tritium as fuel in the future [8], and small, controlled amounts of tritium will be released into the environment from fusion facilities as exhaust gases and drain water.

The major chemical forms of atmospheric tritium are water vapor (HTO), tritiated molecular hydrogen (HT), and hydrocarbons, mainly in the form of CH$_3$T. The atmospheric concentration of tritium changes continuously with time. Recent measurements of tritium concentrations from HTO, HT, and CH$_3$T have been summarized in the literature [4, 9], but almost all the data are averages over long sampling intervals. The atmospheric tritium concentration is expected to be affected by weather conditions (wind speed, wind direction, and washout), environmental water-to-air exchanges (deposition and evaporation), and soil-to-air transfers (re-emission by evaporation). It is therefore important to determine the continuously varying short-term atmospheric tritium concentrations in order to understand the local atmospheric environment and environmental safety around tritium-handling facilities such as a fusion facility. Atmospheric HT and CH$_3$T become oxidized, eventually existing as HTO in the atmosphere. In addition, the effective dosage coefficient for the inhalation of soluble or reactive gaseous forms of HTO (1.8×10^{-11}) is higher than for HT (1.8×10^{-15}) or CH$_3$T (1.8×10^{-13}) [10]. Thus, it is important first of all to determine the short-term

HTO concentrations in the atmosphere. Some researchers have employed a gas-separation membrane module consisting of hollow fiber polyimide films as a gas-separation system for tritium removal [11–14]. Such a module has the advantage of a high ability to separate water vapor from air [15]. Furthermore, it simultaneously purifies the water vapor it is separated from the air. Thus, if we are able to measure the collected water vapor without first having to distill it, we may be able to measure quickly the low-level tritium concentration in samples.

Using such a hollow fiber membrane module, we have now developed a rapid-sampling system for tritium measurements in atmospheric water vapor. In the present paper, we provide an overview of this system and describe its use under experimental conditions. In addition, we report short-time-interval variations in the atmospheric HTO concentration observed near a nuclear facility and its correlation with weather conditions.

2. Materials and Method

We have constructed a rapid-sampling system for experimental measurements of tritium in atmospheric water vapor using a hollow fiber membrane module. This system consists of a high-efficiency particulate air (HEPA) filter cartridge, an oil-free compressor, a water-vapor-separating module with hollow fiber membranes, a cold trap, and an oil-free vacuum pump. We used a UBE membrane dryer (UMS-B5, UBE INDUSTRIES, LTD.) for water-vapor separation (Fig. 1). This module is generally used as a dryer column to generate dry air. The permeance of water vapor through this module is several hundred times greater than that of air [15]. The basic specifications of the module are listed in Table 1.

A schematic diagram of the system is shown in Fig. 2. First, compressed air at 0.4 - 0.7 MPa that is supplied by the compressor (DOP-80SP, ULVAC KIKO Inc.) is introduced into the water-vapor-separation module through
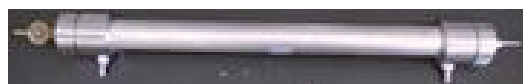
the HEPA filter (GM12144, PALL Corporation, USA). The compressed sample air is supplied to the bore of the hollow fiber membrane; dry air is obtained from the non-permeating side (inside), and wet air (including water vapor) is obtained from the permeating side (outside) due to the difference in the partial pressure of water vapor inside and outside of the hollow fiber membrane. On the side of this module, there is an inlet for purge gas and an outlet for the permeating gas. The purge-gas inlet is closed in the present system, and a difference in the partial pressure of water vapor is produced by evacuating the air from the outside of the membrane filter using a vacuum pump (GVD-050A, ULVAC KIKO Inc., Japan). The total size of this system is approximately H: 800 mm, D: 500 mm, and W: 800 mm. An overview image of this system is shown in Fig. 3. The water vapor permeating through the tubes is collected by two cold traps cooled with dry ice and ethanol. We connected drier column-1 (50 mmϕ) packed with 300 g of the molecular sieve 3A (MS-3A, WAKO, Japan) as a
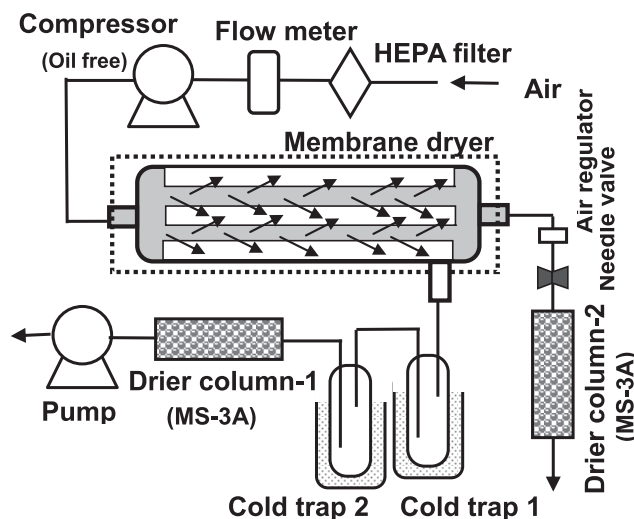

Fig. 2 Schematic diagram of the sampling system for collecting water vapor from air.

Fig. 1 Image of UMS-B5.

Table 1 Basic specification of UMS-B5.

Container material	SUS304
Size (mm)	L: 680, D: 65
Inlet pressure	Max 1.0MPaG
Inlet temperature	1 – 40 ℃
Ambient temperature	1 – 40 ℃
Heatproof temperature	60 ℃

Fig. 3 Image of the test system used in this study.

backup for the cold traps. We heated the module with a flexible heater having a thermal controller (DG2N-100, Hakko Electric Co. Ltd., Japan) to control its temperature. To check the rate of recovery of water vapor, we collected the water vapor remaining in the air that had passed through the module with drier column-2 (which is the same type as drier column-1), and we measured the weight of the column before and after sample collection. We also measured the air temperature and the relative humidity outdoors near the sampling tube, using a portable temperature and humidity meter with a data logger (TR-72nw, T&D) to calculate the absolute humidity $(g\, m^{-3})$.

3. Results and Discussion
3.1 Performance test of the system

We evaluated the recovery yield of water vapor from the air under various sampling conditions. A common operating condition for the polyimide hollow fiber membrane is a feed pressure of 0.3 to 1.0 MPaG [15], and we chose our experimental conditions with reference to these reports [15, 16]. In these experiments, we supplied compressed sample air (outdoor air) to the system, and we varied the pressure of the compressed air from 0.4 to 0.5 to 0.7 MPaG using an air regulator and a needle valve. The module temperature was either fixed at 50°C or was not controlled (i.e., it remained at the ambient room temperature of about 24°C). Recovery yields were determined using the sample water volumes (cold traps 1 and 2) and the total water volume (cold traps 1 and 2 and drier column-1 and column-2). The recovery yields of atmospheric water vapor using this system are shown in Table 2. As these results show, we were able to collect atmospheric water vapor with a recovery yield of 99.4 ± 0.3 % at a feed pressure of 0.5 MPaG and a module temperature of 50°C. As mentioned above, the recovery yield depends upon the difference in the partial pressure of water vapor between the non-permeating side (inside) and the permeating side (outside) of the module. It also depends upon the module temperature, which governs the diffusion speed of the water vapor. This experimental condition appears to be the optimum for collecting the water vapor.

In general, we measure the tritium concentration in the water samples after distillation to remove impurities. How-

ever, one advantage of the hollow fiber membrane module is the high degree of separation of water vapor [17]. We measured the UV absorption spectrum of the collected water to confirm the water quality using a UV–Vis spectrophotometer (V-560, JASCO, USA) to confirm the situation of water (mixing of impurities). We were not able to find the absorption peak in UV range (in the vicinity of 200 nm). This result indicates that we can measure the tritium concentration using a liquid scintillation counter immediately after collecting the water vapor.

3.2 Application to short-term field observations

We employed this system to investigate short-term atmospheric HTO concentrations. We installed it near a nuclear-fuel-reprocessing plant in Japan (40°57′N, 141°21′E). We collected samples of the outdoor air during 5 - 10 February 2007. The sampling interval was approximately 7 h in the daytime and about 17 h at night. The feed pressure was 0.5 MPaG, and the module temperature was 50°C. We determined the integrated flow rate from the relation between the average absolute humidity $(g\, m^{-3})$ and the collected water weight during the sampling period. After water vapor collection, we mixed a 10 mL water sample from the cold trap with 10 mL of the liquid scintillation cocktail (Ultima Gold LLT, PerkinElmer, USA) in a 20 mL, low-diffusion, polyethylene vial. We measured the tritium radioactivity with an ultra-low-level liquid scintillation counter (Quantulus 1220; PerkinElmer, USA) for 1,000 min. We determined the counting efficiencies by using tritium standard water (SRM 4361C, NIST, USA). As shown in Fig. 4, the short-term atmospheric tritium concentration appears to be influenced by the local wind field. We collected local meteorological data, such as wind speed and wind direction, using meteorological observation equipment (AWA2700, Aanderaa Instruments, USA) at ground level near the sampling point.

We found that the atmospheric HTO concentration in-

Table 2 Recovery yields of atmospheric water vapor using this system.

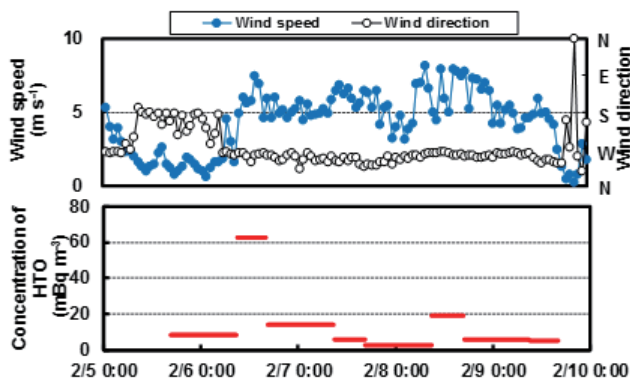| Feed pressure (MPaG)	Module temperature (°C)	Recovery yield (%)	Number
0.4	50	85.7	1
0.5	50	99.4 ±0.3	14
0.5	Room Temp.	94.4 ±1.5	4
0.7	Room Temp.	95.2 ±1.0	3

Fig. 4 Short-term observations of atmospheric HTO concentrations and wind field east of the spent-fuel-reprocessing plant during a test operation using spent nuclear fuel (2007).

creased rapidly because of the air mass transported from the west side of the nuclear facility, but it soon returned to the background level [9]. We have thus demonstrated that our experimental system is capable of measuring short-term variations in atmospheric tritium.

In general, tritium concentrations in the natural environment are known to be high in high-latitude areas and low in areas near the equator [18]. The northwestern monsoon from the Asian continent blows into Japan in winter to spring. And it is reported that tritium concentration in natural water is high in northern Japan and low in southern Japan [19, 20]. Using the system, we have developed, we will plan short-term observations of atmospheric HTO concentrations as an atmospheric tracer in order to study the air mass transportation in northern and southern Japan. And we also plan to collect the tritiated atmospheric molecular hydrogen (HT) as HTO by attaching a catalyst column to this system.

4. Summary

We have developed a rapid-sampling system for tritium measurements in atmospheric water vapor using a hollow fiber membrane module. This system consists of a HEPA filter cartridge, an oil-free compressor, a water-vapor-separating module with hollow fiber membranes, two cold traps, and an oil-free rotary pump. We have shown experimentally that this system can collect water vapor from the atmosphere with a recovery yield of >99 % under conditions of feed pressure 0.5 MPaG and module temperature of 50°C. We were also able to observe changing, short-term, atmospheric HTO concentrations that depended upon the wind field near the nuclear facility. We therefore conclude that our rapid-sampling system can be a useful tool for understanding the short-term variations of tritium in atmospheric water vapor.

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