

Chromatographic Analysis of Molecular Hydrogen (H_2) in the Atmosphere for Understanding Atmospheric Tritiated Hydrogen (HT)*)

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Tritium monitoring would be required at the site of the fusion test facility from the viewpoints of radiation safety and public acceptance. As one of the tritium monitoring items, atmospheric tritium monitoring in the environment is conducted and has three chemical forms: tritiated water vapor (HTO), tritiated molecular hydrogen (HT), and tritiated methane (CH_3T). It is well-known that the specific activity of HT and CH_3T is much higher than that of HTO. To investigate the cause of high specific activity, we focus on the behavior of molecular hydrogen (H_2) in the atmosphere and develop a measurement system based on a gas chromatograph. Monitoring results showed that the range of the H_2 mixing ratio at the NIFS Toki site was 0.4~0.6 ppm over the observation period. Atmospheric H_2 concentrations were higher during the daytime and long daylight seasons, suggesting the generation of hydrogen by photochemical reactions. Preliminary results suggest that there does not appear to be a clear correlation between the concentration of atmospheric HT and the concentration of H_2 in the atmosphere. This suggests that the source of HT is different from the source of H_2 in the atmosphere.

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1. Introduction

Tritium, which is a radioactive hydrogen isotope, is a cosmogenic nuclide produced by the nuclear reactions between the atmosphere (N_2 , O_2) and cosmic rays. The amount of tritium in nature is estimated to be approximately 1-1.3 EBq. On the other hand, the artificial tritium increased due to the atmospheric nuclear bomb testing from 1945 to 1980, and the artificial tritium amount was estimated to be approximately 186 EBq [1]. In recent years, the impact of tritium released from atomic power stations such as heavy water reactor and fuel reprocessing facilities was suggested [1, 2]. In addition, nuclear fusion as the prospective new energy source will become a large tritium release source into the environment.

To understand the plasma physics and progress the fusion reactor development, deuterium gas is utilized as operational gas in the large fusion test device such as Large Helical Device (LHD) in National Institute for Fusion Science (NIFS) and then a small amount of tritium is produced by D-D fusion reaction in the vacuum vessel [3]. Thus, tritium exhausted from LHD would be recovered by an exhaust detritiation system (EDS) [4]. On the other hand, environmental tritium monitoring at the NIFS Toki site is required from the viewpoint of public acceptance.

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At the NIFS Toki site, tritium in river water, pond water, well water, tap water, rainwater, pine needle, and atmosphere has been measured for a few decades [5-7]. As for atmospheric tritium, the chemical forms of tritium are water vapor (HTO), molecular hydrogen (HT), and hydrocarbons (mainly CH_3T) [8-10]. Thus, the atmospheric tritium monitoring system with discriminating chemical forms was developed and the variation of atmospheric tritium at the NIFS Toki site has been observed since 2004 [11]. It is known that the specific activities of HT and CH_3T are orders of magnitude greater than that of HTO. To investigate the cause of high specific activity, we focus on the behavior of molecular hydrogen (H_2) in the atmosphere. Recently, atmospheric H_2 has attracted interest in association with greenhouse gas and from the viewpoint of the creation of a hydrogen energy society. The mixing ratio of H_2 in the atmosphere is reported to be ~0.53 ppm and the lifetime is estimated to be about 2 years. The sources of H_2 are mainly fossil fuel combustion, biomass burning, and the photochemical degradation of organic compounds within the troposphere. The sinks of H_2 are soil uptake by enzymes and microorganisms, and the reaction of H_2 with the OH radical in the troposphere [12-14]. Assuming that the variation of HT is correlated with that of H_2 in the atmosphere, the source of HT would be the same as that of H_2 . In this report, we developed the monitoring system of

trace constituents of the atmosphere, H₂, CO, and CH₄, and then measured them with atmospheric tritium monitoring for a few months.

2. Monitoring System

The development of a gas chromatograph system for continuous trace analysis of H₂, CO, and CH₄ in the atmosphere was based on the reports by Kawano *et al.*, [15,16]. The flow diagram of the gas chromatography system is shown in Fig. 1. The system consists of a gas chromatograph (G2700TF with hydrogen flame ionization detector (FID) for the detection of CH₄, GTR TEC Corporation), an autosampler with a sampling pump and two multiport valves, and trace reduction detector for the detection of H₂ and CO (TRD, J-SCIENCE LAB Co., Ltd.). The sampling control and chromatogram analysis were conducted by HCP software (Version: 5.0.2.354, GTR TEC corporation). The gas separation column was a series of molecular sieves 5A (MS-5A, column length: 2 m) and Porapak-Q (PQ, column length: 2 m). The carrier gas was ultra-high purity nitrogen gas (Purity, >99.99995%). The ultra-high purity hydrogen gas (Purity, >99.99999%) and purified air by passing through a catalyst heated up to 500 °C to burn off all hydrocarbons in the atmosphere were used for FID. The sampling gas volume was 2 cm³. The detection ranges of FID and TRD were more than sub-ppm order for CH₄ and a few ten ppb to 10 ppm for H₂ and CO. The measurement interval was 2 or 3 hr. The height of the monitoring point was 6 m from ground level. To detect the different gas species by two detectors and discriminate oxygen component, 6 ports valve was switched on the way of chromatographic measurement. An example of a chromatogram is shown in Fig. 2. The first large peak is hydrogen, and the second and third large peaks are methane and carbon

monoxide. The chromatogram indicates sufficient retention time for the discrimination of hydrogen, methane, and carbon monoxide. The standard gas of 0.98 ppm of H₂, CO, and 2.0 ppm of CH₄ based on N₂ was used for the calibration of the chromatogram. The calibration operation was conducted once a month and the measurement results were corrected. The gas sampling line of the gas chromatograph system was connected to the sampling line of the original tritium active sampler system. The detailed specifications, operation conditions of the tritium active sampler system, and tritium measurement are described in the reports of Uda *et al.* and Tanaka *et al.* [11,17].

The meteorological observation station was installed on the top of the research staff building at the center of the Toki site. The height of the observation point was approximately 40 m from the ground level. The observation items were wind direction, wind speed, atmospheric pressure, air temperature, humidity, ground temperature, solar radiation, and precipitation. The data acquisition interval

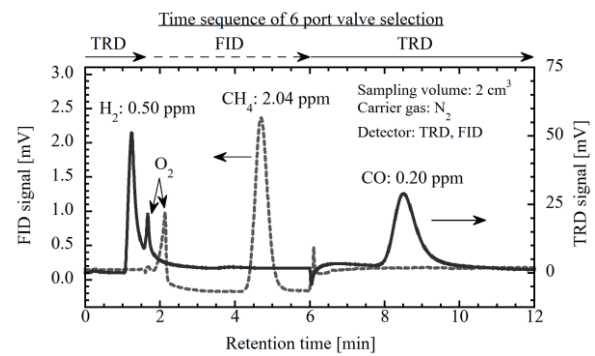


Fig. 2 An example of chromatogram by the gas chromatography using FID and TRD.

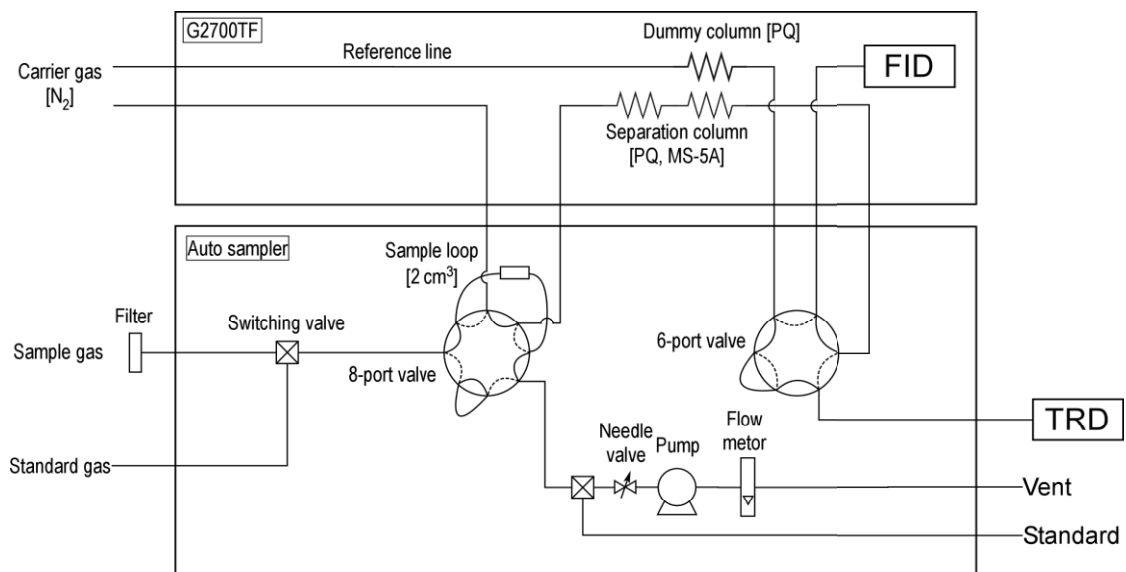


Fig. 1 Schematic diagram of gas flow line in the gas chromatograph and the autosampler.

was set to be 10 seconds.

The NIFS Toki site is located about 100 km inland, north of the Pacific coastal areas, and the buildings stand on a hill at an altitude of about 200 m. The measurement of trace constituents of the atmosphere was started concurrently with atmospheric tritium monitoring in late June 2022.

3. Results and Discussion

The concentration variation of the trace constituents of the atmosphere for four months is shown in Fig. 3. The measurement was interrupted for the separation column conditioning from 4th October to 7th October. Large peak concentration was occasionally observed in all trace constituents. Diurnal and long-term variation of H₂ concentration was observed. The concentrations of CO and CH₄ were not indicated long-term variation and were almost constant.

To clarify the diurnal variations, the concentration at each measurement time in a day was averaged from June to October, and the results are shown in Fig. 4. Here, the time average and integrated solar radiation in a day were also indicated. H₂ concentration was the lowest at 6:00 and then gradually increases during the daytime, and then reached a maximum around 18:00~20:00 at sunset. The solar radiation began the increase at 6:00 and reached a peak at noon. After 18:00, the solar radiation became almost zero. The variation of H₂ concentration seems to correlate with the integrated solar radiation. During the daytime, photochemical reactions are supposed to promote the production of H₂. Then, H₂ uptake in the soil would occur in the nighttime and the H₂ concentration might decrease. On the other hand, CH₄ concentration slightly increased during the nighttime and decreased during the daytime. The variation in CO concentration was similar to that of H₂. They suppose that the correlation between CH₄ and H₂ has negative and the correlation between CO and H₂ has positive. These correlations indicate that the photochemical reaction to produce H₂ in the atmosphere starts from CH₄ or VOC, and then some of the final products are CO and H₂ [14].

Figure 5 shows the variations of monthly mean solar radiation, the concentration of trace constituents in the atmosphere, and HT concentration from June to November. The shorter the daytime toward winter, the lesser the solar radiation. H₂ concentrations reached a maximum in July, and a gradual decrease was observed through the fall. Except for June data, H₂ concentration would be correlated with solar radiation. However, the correlation between H₂ and other species of CO and CH₄ observed in diurnal variation data was not obtained clearly in the monthly mean data. A part of the concentration variation would be caused by the photochemical reactions due to solar radiation as well as the temporary effect due to air mass such as migratory anticyclones and cyclones from the Asian Continent

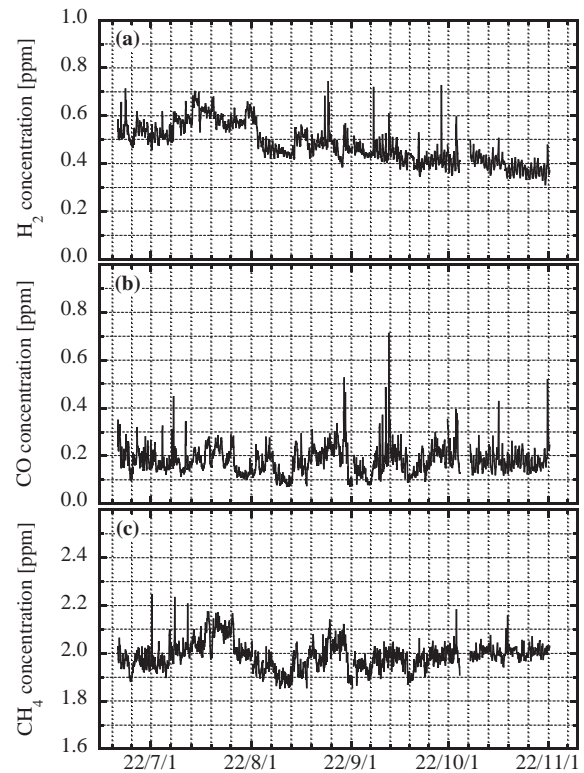


Fig. 3 Concentration variations of trace constituents of the atmosphere at Toki: (a) Hydrogen, (b) Carbon monoxide, (c) Methane.

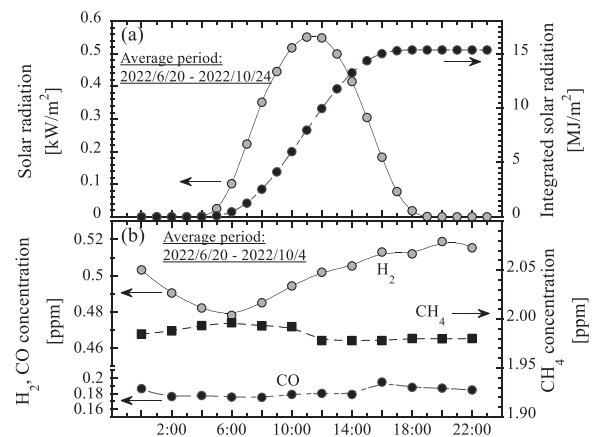


Fig. 4 Average diurnal variations of solar radiation and the concentration of trace constituents of the atmosphere.

and the Pacific Ocean. The air mass transports an atmosphere from another area and mixes with the atmosphere in the observation area. Thus, the seasonal correlation among the species of H₂, CO, and CH₄ may not be observed.

The concentration of atmospheric HT was almost constant during the observation period. Although these data show preliminary results, it seems that the behavior of atmospheric HT concentration is a different trend from that of atmospheric H₂ concentration. To clarify the correlation between HT and H₂ in the atmosphere, long-term monitor-

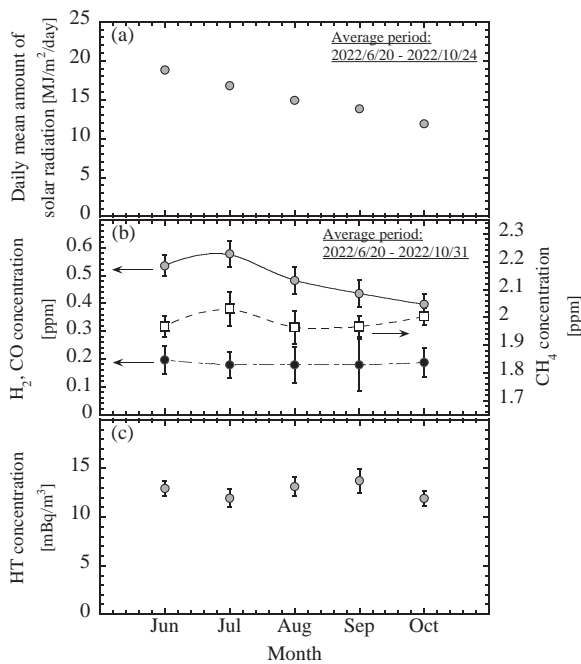


Fig. 5 The variations of monthly mean solar radiation, trace constituents in the atmosphere and molecular tritium (HT): (a) Solar radiation, (b) Concentrations of trace constitution in the atmosphere, (c) Atmospheric HT concentration.

ing of more than one year is required.

4. Conclusions

To understand the behavior of atmospheric molecular tritium (HT), a chromatographic analysis of trace constituents (H_2 , CH_4 , CO) of the atmosphere was conducted using a gas chromatograph with a trace reduction detector (TRD) and hydrogen flame ionization detector (FID) at Toki, Japan. H_2 concentrations in the atmosphere were higher during the daytime and the season with long day-

light hours, suggesting hydrogen production by photochemical reactions.

As the preliminary result, there does not appear to be a clear correlation between atmospheric HT concentrations and atmospheric H_2 concentrations. It suggests that the source of molecular tritium is different from that of the molecular hydrogen in the atmosphere. For future studies, long-term observational data are needed to obtain clear conclusions.

Acknowledgments

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