Water Collection on a Platinum-Coated Molecular Sieve

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Abstract

Tritium is a radioactive isotope of hydrogen gas that is used regularly in experiments at the Laboratory for Laser Energetics (LLE). To prevent emissions to the environment, capture and containment of tritium released from process systems is very important. Air detritiation systems oxidize elemental tritium to form tritiated water (HTO), which is then collected on a molecular sieve drier. Tests were conducted to determine whether or not a platinum-coated molecular sieve (Pt/4A MS) loaded with light water (H_2O) could serve as an alternative to the classical 'burn and dry' approach of capturing tritiated water currently employed (1). In these tests, deuterium was used as a surrogate for tritium. Deuterium gas in a helium carrier was converted to heavy water over a hot copper/zinc getter bed (2,3) and flowed over a platinum-coated 4A molecular sieve preloaded with light water. The dependence of the amount of heavy water captured in the molecular sieve on flow rate was measured.

1. Introduction

Currently, at LLE, the tritium removal from Omega and processes that contain tritiated air utilize the conventional "burn and dry" detritiation method (4). This comprises the conversion of elemental tritium to oxide using hot copper oxide, Hopcalite, or a precious metal catalyst (Pd, Pt), a molecular sieve drier and a tritium monitor. Although this system serves its purpose, conversion of HT to water over Hopcalite requires the presence of oxygen. A novel method of detritiation, explored in these experiments, may offer a simpler and more versatile solution. A platinized molecular sieve (Pt/4A MS) preloaded with light water (H_2O) may eliminate the need for an oxidizer and drier. These two options are illustrated in Figure 1. In cases where the water content in the air stream is high, a condenser can be installed in front of the drier to extend the operational lifetime of the drier as shown in Figure 1.

In this experiment, a Pt/4A MS was tested for its ability to remove tritiated water (T_2O) from an air stream with high humidity. The purpose of this experiment was to determine whether or not a Pt/4A MS, preloaded with H_2O, could adsorb a significant amount of T_2O, using D_2O as a surrogate. The efficiency and capacity at different flow rates of deuterium were also tested in the experiments.

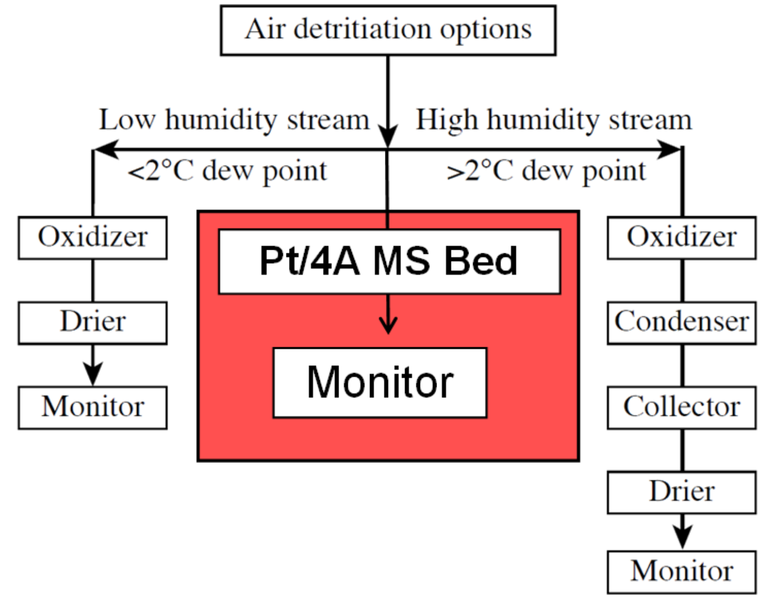

Figure 1: Schematics of air detritiation systems.

2. Experimental

2.1. System Configuration

A system was built to test how much D_2O could be loaded on to a Pt/4A MS, preloaded with H_2O. The system is organized into three sections: D_2O production, isotopic exchange, and hydrogen/deuterium detection. As seen in Figure 2, there are four gas cylinders containing He, 1% O_2 in He, D_2, and compressed air. The gases, whose flow rates are controlled by mass flow controllers (MFC), are flowed either through a bed or through a bypass. The gases are monitored downstream of both beds by the atmospheric sampling system, including a diaphragm pump, a turbomolecular pump, and a residual gas analyzer (RGA). An RGA measures the partial pressures of gases in the system. The nitrogen partial pressure was measured to ensure that no air leaked into the system during loading of the Cu/Zn getter bed. The total pressure could also be measured. A dew point sensor measured the humidity of the compressed air being flowed into the system. Thermocouples were used to control the temperatures of the Cu/Zn getter bed, the Pt/4A MS bed, and the heating tape used around the capillary tubing as well as select areas of piping. Capillary tubing connects the system with the RGA/ Atmospheric Sampling System and allows sampling during the experiments.

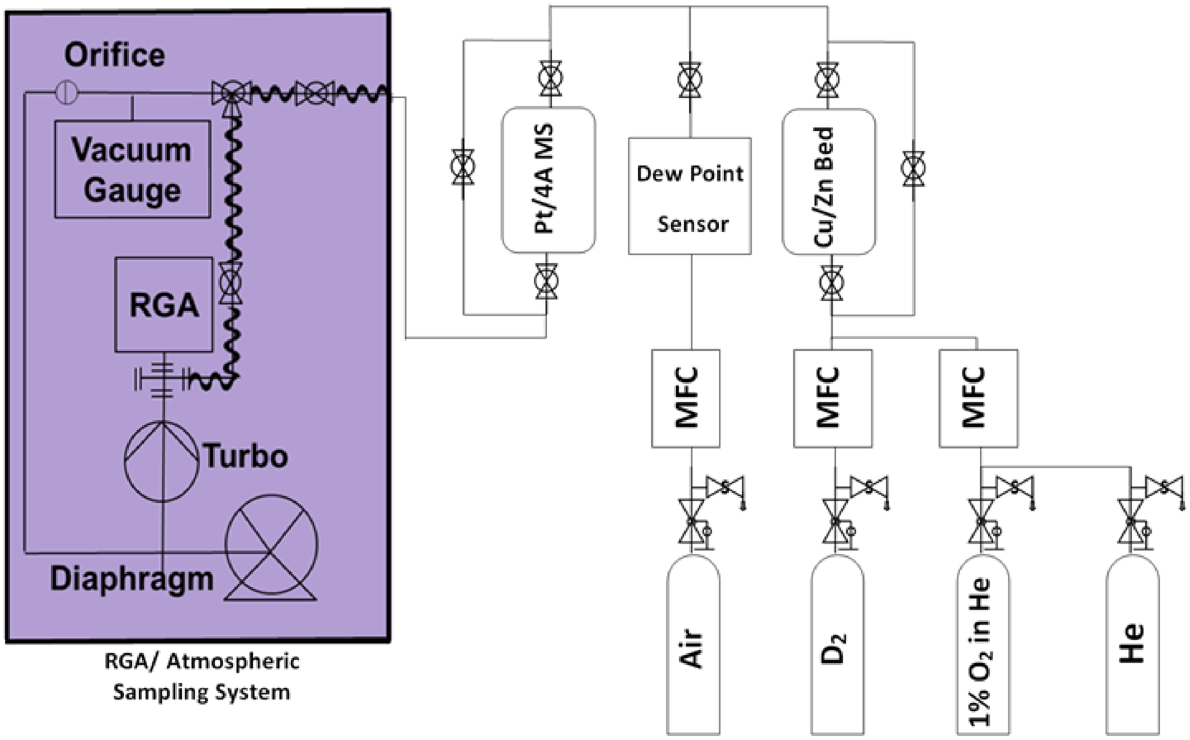

Figure 2: Schematic of experimental system. Capillary tubing is represented with the bolded, squiggly line.

2.2. Experimental Procedure:

2.2.1 Formation of D_2O:

The Cu/Zn getter bed was heated to 200°C , and 1% O_2 in He was flowed at 5 LPM (liters per minute) through the bed. The Pt/4A MS bed was bypassed such that no oxygen flowed through it. Once filled to capacity, the getter bed was bypassed, and He was flowed at 5 LPM to purge the system. Once the system was purged, the Cu/Zn getter bed was re-opened and D_2 was flowed through it at 50 sccm (standard cubic centimeters per minute). As seen in Figure 3, a stream of D_2O was produced for approximately 500 minutes before D_2O production began to decrease. This occurred when the oxidized Cu/Zn was reduced to elemental Cu/Zn and no more O_2 was available. Because the stream of D_2O was not continuous over a long period of time, this method of D_2O production was referred to as the “limited production method”.

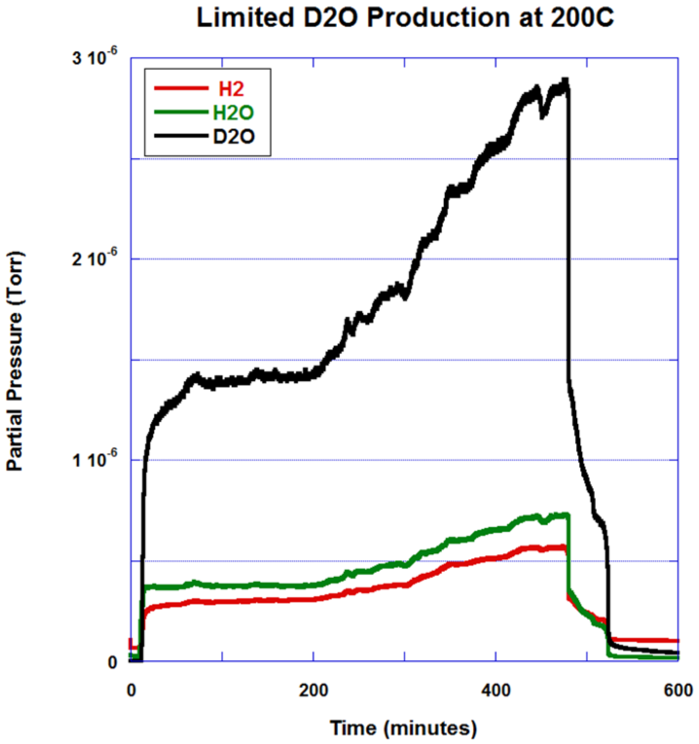

Figure 3: H_2, H_2O, and D_2O partial pressures as functions of time when D_2 was flowed at 50 sccm through a Cu/Zn getter bed loaded with O_2. The Cu/Zn bed was heated at 200°C.

It was found that this method of D_2O production would not suffice for full runs, a full run meaning an experiment where D_2O is flowed through a Pt/4A MS bed preloaded with H_2O until complete D_2O breakthrough occurs from the Pt/4A MS bed without running out of D_2O on the Cu/Zn bed. Instead, it was determined that a constant stream of D_2O would be necessary. To produce a constant, unlimited flow of D_2O, D_2 and 1% O_2 in He were co-injected into the system through the Cu/Zn getter bed, which was preloaded to capacity with O_2. D_2 was flowed at 100 sccm and 1% O_2 was flowed at 5 LPM. This method, referred to as the "continuous production method," proved to be successful. As seen in Figure 4, a stable D_2O stream leaving the bed approaches a steady state level after approximately 300 minutes.

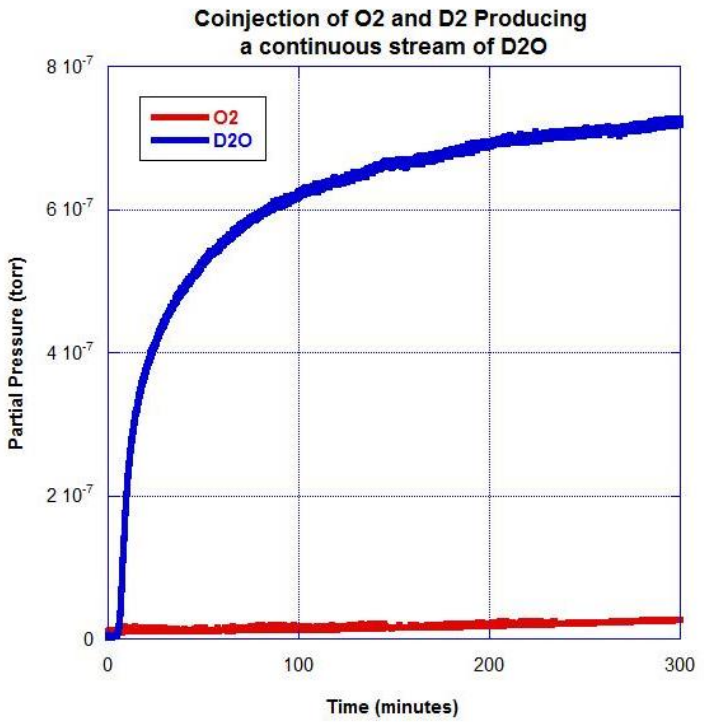

Figure 4: Partial pressures of D_2O and O_2 as functions of time when D_2 and O_2 were simultaneously flowed through the Cu/Zn getter bed. D_2 was flowed at 100 sccm. O_2 was flowed at 5 LPM. The Cu/Zn getter bed was preloaded with O_2 and kept at 200°C.

2.2.2 Loading Pt/4A MS with H_2O:

To prepare the Pt/4A MS for operation in humid air streams, the Pt/4A MS bed was pre-loaded with H_2O. This medium was chosen because of its ability to capture H_2O. The interatomic space between the neighbor cages of the molecular sieve is four-angstrom. Four angstrom molecular sieves have the ability to adsorb H_2O without altering its chemical composition, allowing it to extract H_2O from flowing gas streams. When loading the Pt/ 4A MS with H_2O, the Cu/Zn getter bed was valved so as to isolate the Cu/Zn getter from the H_2O. Initially, compressed air was flowed at 1 LPM, such that a 100% air flow pressure was recorded for later comparison. The air flow was turned off, and He was flowed at 1 LPM to purge the system. The Pt/4A MS bed was opened, still only flowing He at 1 LPM. Once air levels were back down to background levels, the He flow was stopped and the air flow was turned on at 1 LPM.

2.2.3 Full Experiment:

Once the system was set up for a full experiment (i.e. the Cu/Zn bed was loaded to capacity with O_2 and the Pt/4A MS was loaded with H_2O), co-injection of D_2 and 1% O_2 in He began through the Cu/Zn getter bed which was preheated to 200^oC . Once a stable maximum reading of D_2O production was recorded, the Pt/4A MS bed was opened and its bypass closed. Full runs were performed at three different flow rates of D_2. After a full run was completed, the system was purged and reset. To purge the system, the Pt/4A MS was heated to 150^oC, and He was flowed through it at 2 LPM. After 120 minutes, the temperature of the Pt/4A MS was increased to 200^oC.

3. Results:

The results of one run using the limited production method are shown in Figure 5. The results show that D_2O can, indeed, be stored on the loaded Pt/4A MS, and that the Pt/4A MS is capable of adsorbing significant amounts of D_2O. The amount of D_2O is comparable to the amount of H_2O that can be stored. Prior to a full test, approximately 8g H_2O /gMS was loaded onto the Pt/4A MS. When D_2O was flowed through the pre-loaded Pt/4A MS using the limited production method, approximately 5g of additional D_2O/g MS was loaded onto the Pt/4A MS.

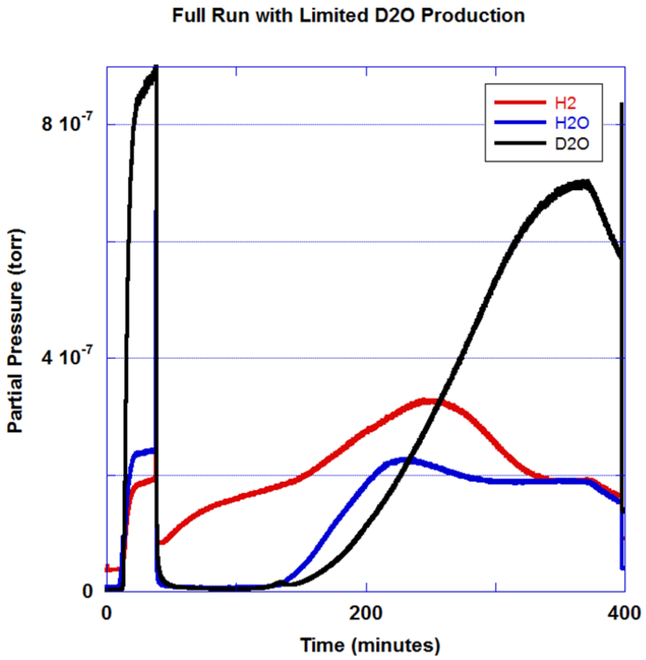

Figure 5: Partial pressures of H_2, H_2O, and D_2O as functions of time in an experiment to test the ability of the Pt/4A MS to capture D_2O. D_2O is flowed through the pre-loaded Pt/4A MS starting at 40 minutes. The D_2O was created by flowing D_2 at 50 sccm through a Cu/Zn getter bed loaded with O_2. The getter bed was kept at 200°C and the Pt/4A MS was kept at ambient temperature (20°C). A stable maximum reading of D_2O was recorded before the test began, for later comparison.

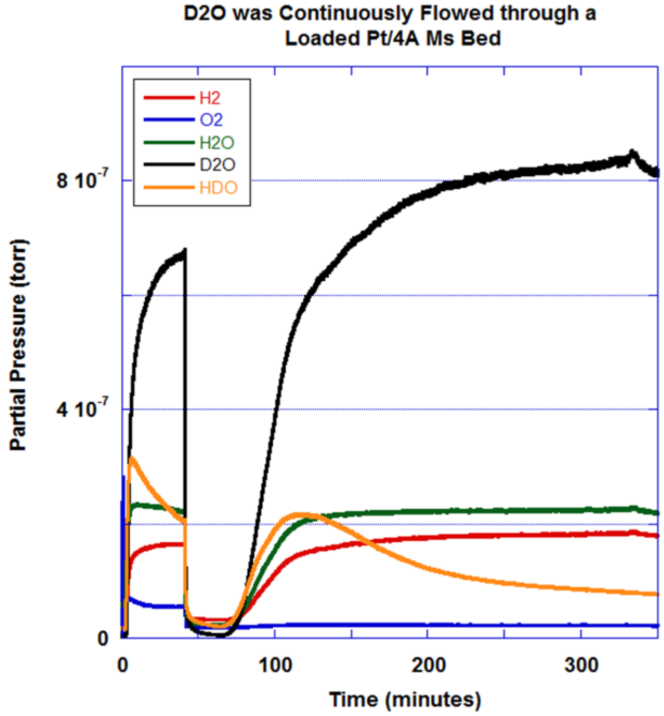

Figure 6: Partial pressures of H_2, O_2, H_2O, D_2O, and HDO as a function of time for an experiment similar to that of Figure 5 except that 1% O_2 in He was also flowed through the Cu/Zn getter bed. D_2 was flowed at 100 sccm. O_2 was flowed at 5 LPM. At 40 minutes, the Pt/4A MS was opened and D_2O was allowed to flow through the Pt/4A MS.

High capture efficiencies were realized at superficial flow rates up to 11 scc/min/cm^2. In Figure 6, D_2 was co-injected with 1% O_2 in He at the respective rates of 100 sccm and 5 LPM. For 27 minutes, no D_2O was recorded in the outlet stream, indicating that all D_2O being produced was being absorbed by the Pt/4A MS. 27 minutes into the experiment, however, breakthrough occurred. Breakthrough refers to the time at which the concentration of D_2O in the outlet stream reaches 1% of the value when the bed is bypassed, or, in this case, $2.31\text{x}10^{-9}$ torr. For the remainder of the experiment, the Pt/4A MS's ability to absorb D_2O decreased until the maximum reading in the outlet stream was reached.

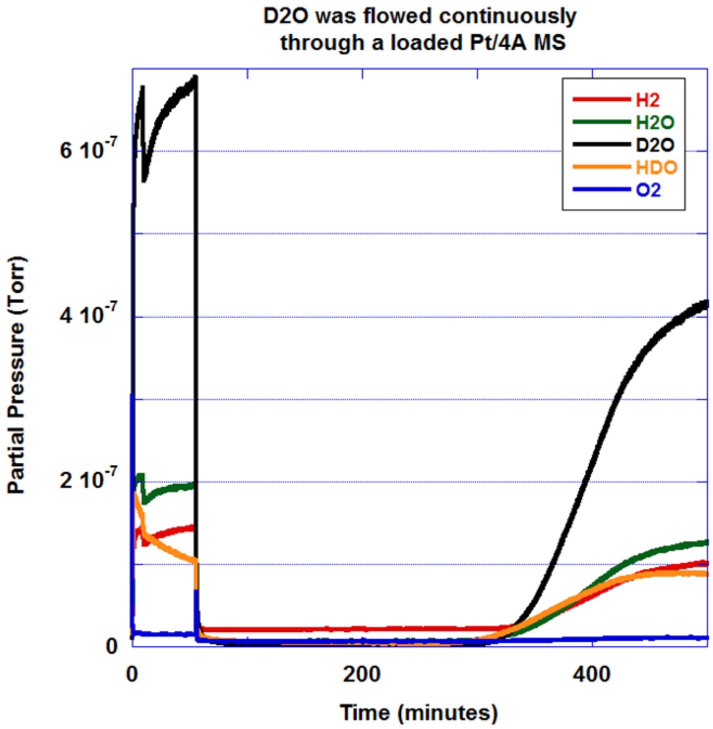

Figure 7: Partial pressures of H_2, O_2, H_2O, D_2O, and HDO as a function of time for an experiment similar to that of Figure 6 but with lower D_2 and O_2 flow rates. D_2 was flowed at 20 sccm. O_2 was flowed at 1 LPM. At 40 minutes, the Pt/4A MS was opened and D_2O was allowed to flow through.

As shown in Figure 7, the same experiment was performed with D_2 flowing at a lower rate of 20 sccm, and 1% O_2 in He flowing at a rate of 1 LPM. In this experiment, breakthrough occurred 260 minutes into the experiment. The mass of D_2O loaded onto the Pt/4A MS is shown in Table 1. Reducing the D_2O residence time in the Pt/4A MS by a factor of 5 increases the storage capacity approximately two fold, even though the Pt/4A MS has been preloaded with H_2O to capacity.

Flow Rate of D_2O (sccm)	Mass of D_2O Loaded onto Pt/4A MS (gD_2O/gMS)
20	2.4
100	4.7

Table 1: Total mass of D_2O loaded onto Pt/4A MS for runs at both D_2O flow rates of 20 sccm and 100 sccm.

Conclusions

Experiments were performed to determine whether a Pt/4A MS could serve as a novel and alternative method to the conventional “burn and dry” method for tritium extraction from a humid air stream. Tests were completed by flowing D_2O through a Pt/4A MS preloaded with H_2O, to simulate the humid air stream. Superficial flow rates were realized up to 11 scc/min/cm^2. Results indicate that the Pt/4A MS has the capability of capturing up to 4.7g/g MS of D_2O on a bed preloaded to capacity with H_2O. These tests suggest that a simpler, more versatile technique of tritium capture and recovery can be implemented at LLE by preferential extractions of HTO from humid airstreams.

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