Capturing Hydrogen on Chilled Molecular Sieve

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I. Abstract

LLE studies inertial confinement fusion using deuterium-tritium fuel mixtures. Tritium released from processing equipment is re-captured with *ZrFe* getter beds. These devices must be unloaded annually to recover their tritium collection efficiency. One approach to collecting the tritium released from *ZrFe* getter beds utilizes a cryotrap, a coil filled with crushed molecular sieve chilled to liquid nitrogen temperatures (77 K). The performance of a compact cryotrap was evaluated using hydrogen-helium mixtures. The hydrogen capacity of the cryotrap has been measured to be 5.99 sL, or 58.5 scc of hydrogen per gram of molecular sieve. At approximately one-fifth of the total capacity, the mean residence time of the hydrogen in the cryotrap is 170 minutes for a helium purge flow rate of 0.100 L/min. The residence time decreases logarithmically as the helium purge flow rate increases. The cryotrap releases deuterium before it releases hydrogen, and the deuterium residence time has a linear relationship with the helium purge flow rate.

II. Introduction

The University of Rochester's Laboratory for Laser Energetics (LLE) operates a 30 kJ laser to study inertial confinement fusion reactions that utilize deuterium-tritium (*DT*) fuel mixtures inside cryogenic targets. Typically, *DT* fuel needs to be pressurized to several hundred atmospheres and then cooled below the triple point of 19.8 K to form a layer of *DT* ice inside the thin plastic target shells. The tritium processing equipment required to generate these high pressures and low temperatures is encapsulated in a glovebox in order to minimize the release of tritium to the environment. This glovebox system *(see figure 1)* is continuously flushed with helium, which then encounters a series of adsorbent beds in order to remove tritium effluents
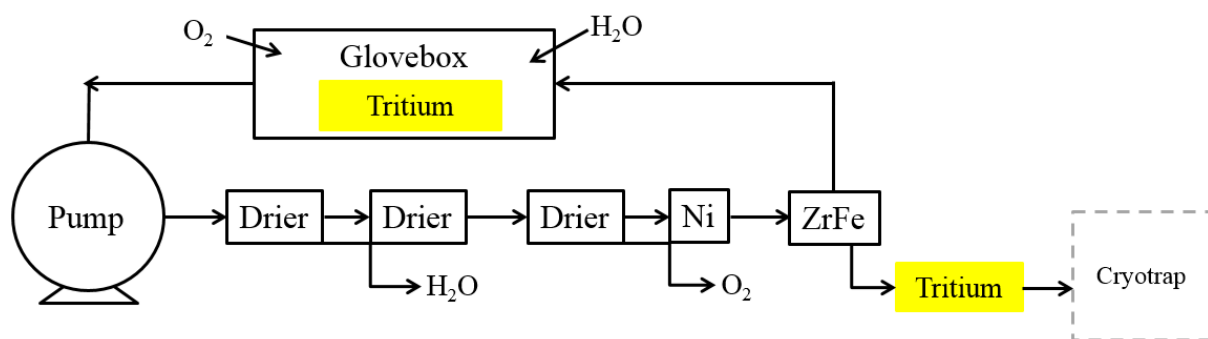
Figure 1. Schematic of the glovebox environment containing tritium processing equipment. The first two driers remove water from the helium stream and the next two beds remove oxygen from the stream in order to protect the ZrFe bed from oxidization. The ZrFe bed removes tritium, which could potentially be unloaded into a cryotrap.

from the helium stream. The first and second driers in this system remove water from the helium stream. The next two beds consist of a drier that contains room temperature molecular sieve and a nickel bed that remove the oxygen from the stream. These beds are necessary to protect from contaminants that cause passivation of the reactivity of the zirconium-iron (*ZrFe)* bed.[1] The helium stream then flows over the *ZrFe* bed, which removes any traces of tritium that are released from the processing equipment into the helium stream. The *ZrFe* bed must be regenerated annually in order to regain its tritium capturing efficiency. When heated to 450°C and back-flushed with a pure helium stream, the *ZrFe* bed will gradually release the tritium it contains at low concentrations. Currently, the tritium released from these beds is oxidized, transforming it into tritiated water, and collected on molecular sieve driers. These driers are heated off-site to recover the tritiated water that is then reduced in a catalyst column back into deuterium-tritium gas (*DT*). The *DT* is sent to an Isotope Separation System (ISS) where it is purified into tritium and reused. However, if the *DT* released from the *ZrFe* beds could be captured as deuterium-tritium gas without conversion to tritiated water first, then the *DT* gas

could be sent directly to an ISS, simplifying the tritium regeneration process while simultaneously saving money and processing time.

A possible approach to capturing the tritium released from the *ZrFe* beds as tritium gas is by using a cryotrap. A cryotrap is composed of three separate coils that are nested and brazed together. One side contains a heater, the other allows for liquid nitrogen flow, and the coil in the middle of the two contains crushed molecular sieve. When chilled to 90 K, the cryotrap will extract tritium from a helium stream at very low partial pressures and store it on the molecular sieve surface through physisorption. When heated above 110 K, the cryotrap will release the tritium back into the carrier stream at much higher partial pressures. At these higher concentrations, the tritium can be transferred from the cryotrap to a uranium bed for temporary storage or subsequently unloaded into an ISS.

In order to characterize the cryotrap, two sets of trials were conducted. The first consisted of loading hydrogen onto the cryotrap to calculate the cryotrap's maximum hydrogen capacity. The second set of trials measured the maximum residence time for hydrogen to elute from the cryotrap, i.e., the time it takes for the loaded hydrogen to be forced out of the cryotrap by a pure helium purge stream while still cooled at 90 K, at approximately 21% of its hydrogen capacity.

III. Characterization of the Pd/Ag Membrane

In order to determine the time of breakthrough, i.e., the time when the cryotrap stops adsorbing the hydrogen from the helium-hydrogen mixture, it is necessary measure the partial pressure of hydrogen exiting the cryotrap. Because residual gas analyzers and Bayard Alpert gauges are harmed at high pressures, the hydrogen must be separated from the helium stream and then measured. To do so, a heated palladium-silver (*Pd/Ag*) membrane (a permeator) is used.

When a hydrogen-helium mixture is exposed to such a membrane heated to 250°C, hydrogen molecules disassociate into atoms on the membrane surface, are adsorbed into the membrane, permeate through the membrane, re-associate, and are released on the downstream side.[2] Since helium cannot diffuse through the membrane in 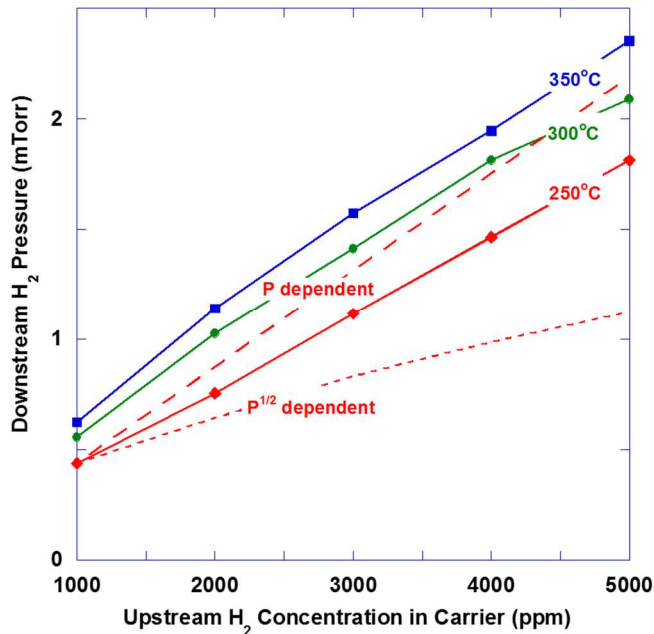this manner, the permeator can be used to separate hydrogen from a helium stream. Testing hydrogen-helium mixtures at various concentrations confirmed that the pressure on the downstream side of the *Pd/Ag* membrane is sensitive to the hydrogen concentration of interest.[3] *Figure 2* shows that in the temperature range 250°C to 350°C the permeator is neither linearly dependent on upstream pressure nor dependent on the square root of pressure, but rather in transition between the

Figure 2. Downstream pressure as a function of upstream hydrogen concentration. As hydrogen concentration increases, so too does upstream pressure; hydrogen concentration in the carrier stream is therefore used as a measure for upstream hydrogen pressure. The relationship between the two proves that the Pd/Ag permeator is sensitive to hydrogen concentration, and therefore allows for the detection of hydrogen in helium streams.

two extremes.[2] Linear dependence on pressure implies that the quantity of hydrogen passing through the permeator depends on the arrival of hydrogen at its surface while dependence on the square root of upstream pressure implies that hydrogen permeation is limited by the diffusion

rate through the palladium-silver tubes. Therefore, during each trial the *Pd/Ag* membrane was

heated to 250°C or above, to prevent the system from falling into a $P^{1/2}$ dependent state.

IV. Experimental Setup

A typical cryotrap run begins by cooling the cryotrap to below approximately 103 K

(-170°C) by beginning the liquid nitrogen flow while flowing a pure helium stream through the

cryotrap. Concurrently, the *Pd/Ag* membrane is heated to approximately 250°C. The temperature

of the entire system is measured in five places using thermocouples. Once below the cyrotrap

temperature threshold, the bypass is closed, and hydrogen is added into the helium stream at a concentration set through the two mass flow controllers (MFCs) *(see figure 3).* The cryotrap is loaded until breakthrough occurs, i.e., until hydrogen stops being adsorbed by the cryotrap because its maximum capacity has
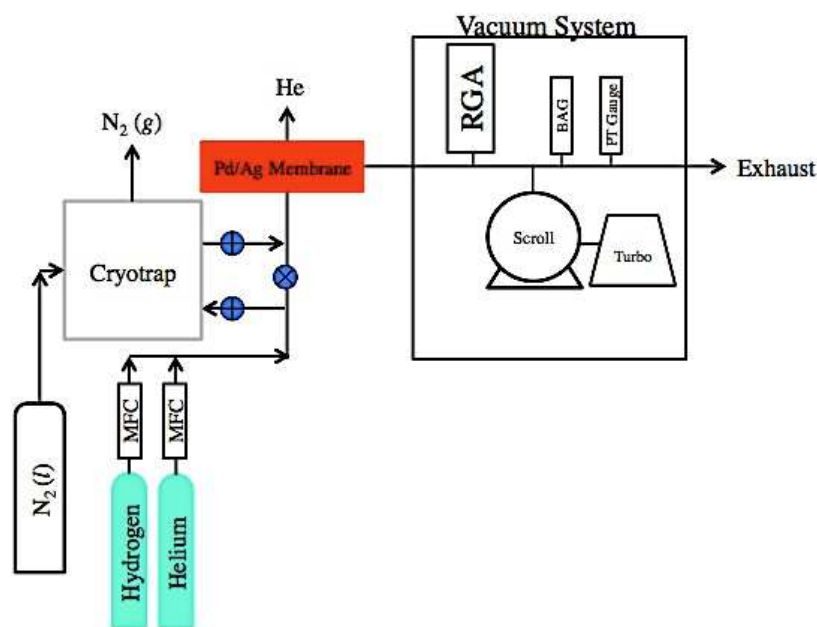

Figure 3. Schematic of experimental setup with the bypass in the closed position. Two separate mass flow controllers (MFCs) control the concentration of hydrogen in the helium stream. The hydrogen that permeates the Pd/Ag membrane enters a vacuum system where it is analyzed by a residual gas analyzer (RGA), which uses an RF-quadrupole mass spectrometer, a Bayard Alpert gauge (BAG), and pressure transducer gauges (PT Gauge). The vacuum system is maintained at approximately 10^{-6} Torr using scroll and turbomolecular pumps.

been reached. At this time, hydrogen comes in contact with the *Pd/Ag* membrane, traverses the

membrane, enters the vacuum system, and is detected by pressure gauges. Inside the vacuum

system, the data collected from a Bayard Alpert gauge (BAG), a 1 Torr pressure transducer gauge, and a 10 Torr pressure transducer gauge are used to create a hydrogen release profile for the run *(see figure 4a).* The total volume of hydrogen loaded onto the cryotrap is calculated using the hydrogen flow rate and the loading time.

During certain trials, the cryotrap capacity decreased because of contact with impurities. However, by attaching heaters to the thermocouples on the cryotrap and heating it to 250°C with a pure helium purge, the cryogenic molecular sieve capacity can be regenerated.[1]

V. Results and Discussion

i. Full Capacity Cryotrap Run

The maximum capacity cryotrap run successfully loaded a total of 5.99 sL of hydrogen onto the cryotrap, giving a capacity of 58.5 scc of hydrogen per gram of molecular sieve contained in the cryotrap. The run began by heating the permeator to 250°C, with a pure helium stream flowing through the bypass at 0.103 L/min, and cooling the cryotrap to 91.0 K (-182.0°C) by starting liquid nitrogen flow. Once both temperature thresholds were reached, the bypass was closed and the cryotrap was opened. At 3 minutes, hydrogen was
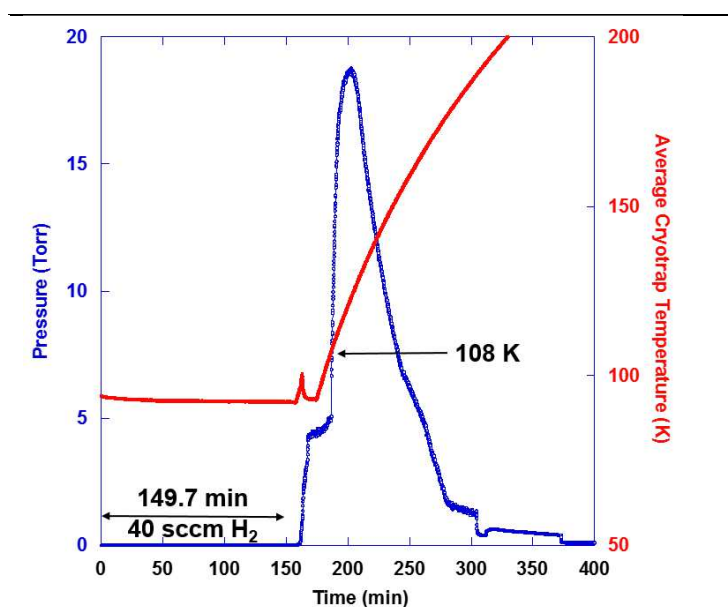

Figure 4a. Hydrogen pressure (Torr) as a function of time. The maximum capacity cyrotrap run was loaded at a flow rate of 40 sccm of hydrogen for 149.7 minutes. At 108 K, the majority of the hydrogen unloaded rapidly. The rapid pressure increase from 158-172 minutes levels at the new baseline pressure of 4.42 Torr.

added into the helium mixture at 40 sccm to create a concentration of approximately 40%. At

149.7 minutes, breakthrough occurred *(see figures 4a, 4b)*, i.e., the cryotrap reached maximum

capacity. The hydrogen flow was shut off at 152 minutes, and the turbomolecular pump was

shut down at 158 minutes to prevent it from overheating. After the pressure in the vacuum

system stabilized to a baseline of 4.42 Torr, at 172 minutes the liquid nitrogen flow was stopped,

and the helium flow rate was increased to 1.002 L/min to facilitate the hydrogen unloading cycle.

Because it proved unreliable at high pressures, the RGA was shut down at 185 minutes. The

cryotrap unloading cycle peaked at 187 minutes at a temperature of 108 K (-165°C). At 239

minutes, the helium purge rate was lowered to 0.100 L/min, and the system was allowed to
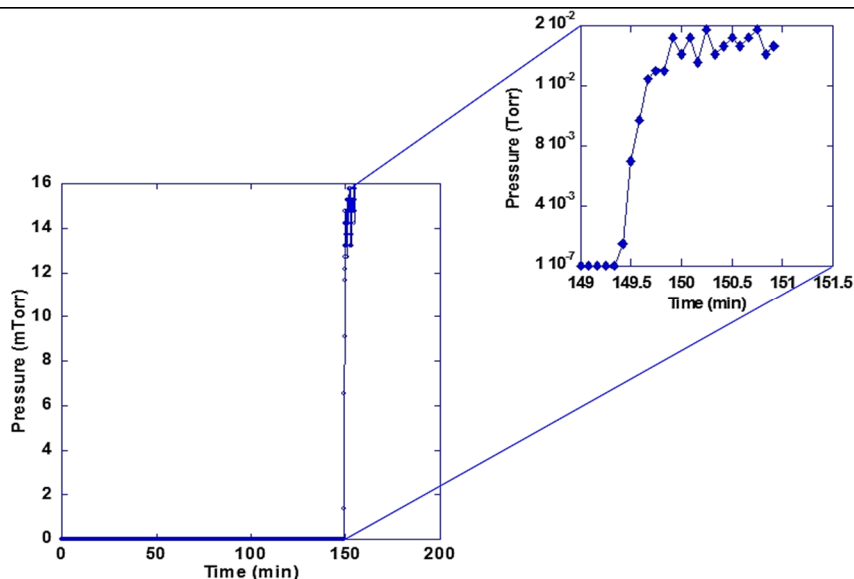
unload overnight.

Figure 4b. A close up of the breakthrough in figure 4a: hydrogen pressure as a function of time. Until breakthrough, the cryotrap is completely efficient at retaining hydrogen.

At breakthrough, 149.7 minutes, no additional hydrogen is adsorbed by the cryotrap

because the cryotrap has reached its maximum capacity. As seen in *figure 4b*, the pressure

gauges initially register a hydrogen signature in the magnitude of 10^{-6} Torr. These pressures are well below the detection threshold of the pressure gauges monitoring the vacuum system. Therefore, it was concluded that until the point of hydrogen breakthrough, the cryotrap is 100% efficient at adsorbing hydrogen. Furthermore, the cryotrap was able to concentrate the release of hydrogen to a maximum of 18.6 Torr. The ability to concentrate tritium is ideal in a tritium recovery method.[4] For example, uranium beds have a high tritium storage capacity; however, they cannot be loaded at the low pressures that are produced when a *ZrFe* bed is purged.[1] Because of its capacity to concentrate, a cryotrap presents a model solution to this dilemma.

ii. Partial Capacity Cyrotrap Run

Tests with the cryotrap charged to full capacity lead to the hypothesis that the cryotrap cannot hold hydrogen indefinitely while cold, if a helium stream is still flowing through the coil. The cryogenic molecular sieve medium does eventually release hydrogen even while chilled to 77 K while being purged with helium.[1] Therefore, for these tests, the cyrotrap was loaded to approximately one-fifth its capacity (1.2 sL), the hydrogen stream was stopped, and a pure helium purge was continued while liquid nitrogen was flowed to maintain the cryotrap's temperature below the normal release threshold (approximately 113 K, or -160°C).
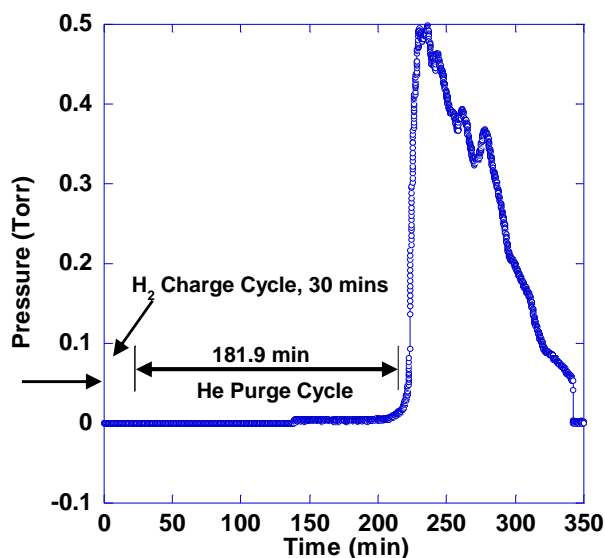

Figure 5. Hydrogen pressure as a function of time measured using pressure transducer gauges. After a 30-minute charge cycle, a pure helium stream at a flow rate of 0.200 L/min takes 181.9 minutes to begin the involuntary unloading of hydrogen from the cryotrap. Unloading was complete after 132.6 minutes.

For a helium purge rate of 0.200 L/min, the cryotrap bypass was opened, the liquid nitrogen flow began to bring the cryotrap temperature down to -178°C (95 K), and the permeator temperature was set to 250°C. The cryotrap bypass was then closed and the hydrogen was added to the helium stream at 40 sccm. At 30 minutes, after 1.2 L of hydrogen had been loaded, the hydrogen flow was stopped. With the cryotrap temperature below 95 K, the helium purge took 182 minutes to push the hydrogen through the entire length of the cryotrap and out the other end *(see He purge cycle in figure 5).* At 212 minutes, the helium purge forced hydrogen breakthrough. The hydrogen unloading cycle was completed at 345 minutes. Repeated partial capacity trials revealed a trend between hydrogen residence time (the time it takes for the hydrogen to exit the cryotrap), t_H, and helium purge flow rate, σ, given by the following equation, as illustrated in *figure 6*:

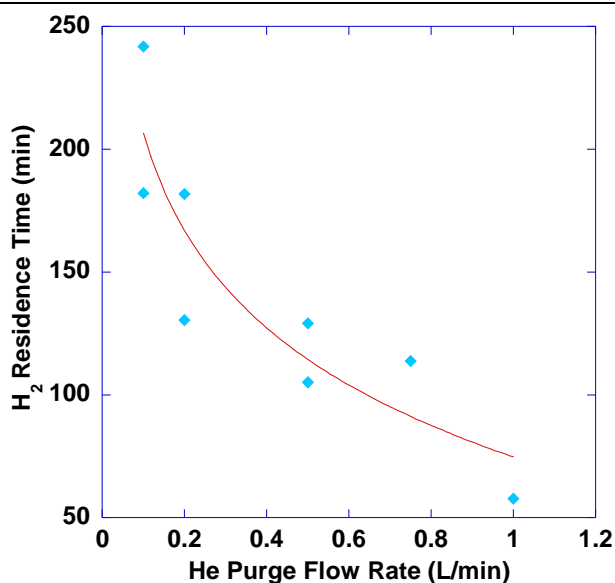$$t_H = -131.9 \, log(\sigma) - 74.8 \qquad [1].$$

Figure 6. Hydrogen residence time as a function of helium purge flow rate. There is a noticeable logarithmic relationship between the helium purge rate and the residence time of the 1.2 L of hydrogen inside the cryotrap. $R^2 = 0.802$

10

Returning to the first partial capacity run, an unexpected increase in pressure *(too minute to be visible in figure 5)* was noticed at 115.5 minutes (85.5 minutes after the hydrogen loading cycle was completed). Cryogenic molecular sieves were once used to separate hydrogen isotopes, and there are approximately 150 ppm of deuterium naturally occurring in hydrogen. Therefore, hydrogen-deuterium traces were tested for during these runs to determine if deuterium was released first during this miniscule pressure increase. Hydrogen-deuterium (*HD*) was monitored because any deuterium passing through the permeator would be more likely to recombine with hydrogen atoms because of their relative abundance. Thus, by monitoring *HD* releases, the deuterium residence time can be determined. Using the RGA, it was confirmed that the initial breakthrough, i.e., the first pressure increase at 115.5 minutes, is a release of hydrogen-deuterium molecules (*HD*). As shown in *figure 7*, the concentration of *HD* overtakes the concentration of hydrogen entering the vacuum system. Furthermore, this initial breakthrough point was determined for multiple helium flow rates, revealing a linear dependence on helium purge flow rate modeled by the equation *(figure 8):*

$$t_D = -171.0\sigma + 146.7 \qquad [2]$$

where helium purge flow rate is σ and deuterium residence time is t_D.

These relationships between helium purge flow rate and deuterium residence time are significant for the cryotrap's implementation. Although deuterium is only a small fraction of naturally occurring hydrogen, there is importance in investigating its properties because the eventual application of the cryotrap will be storing both deuterium and tritium. These equations hypothetically give an estimated timeframe for handlers to set up a uranium bed or the ISS at the end of the cryotrap. After the set amount of time for the helium purge flow rate has elapsed, the

cryotrap will involuntarily release its contents. Therefore, the cryotrap must undergo further tests using deuterium and tritium.
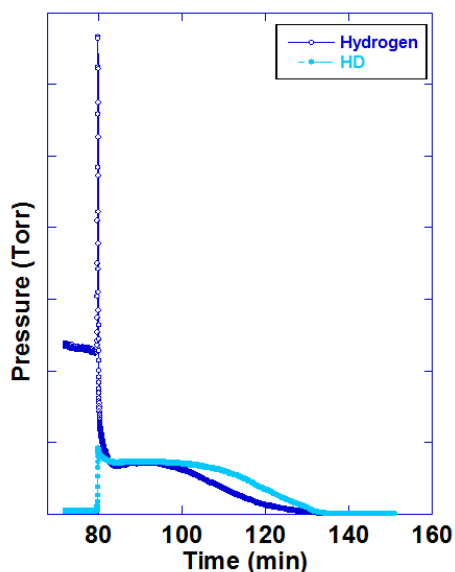

Figure 7. Pressure as a function of time. During the initial breakthrough (the pressure increase at 115.5 minutes), deuterium has a greater presence than hydrogen. Because the RGA is overloaded at high pressures, the pressure appears to decrease at breakthrough when it is actually increasing.
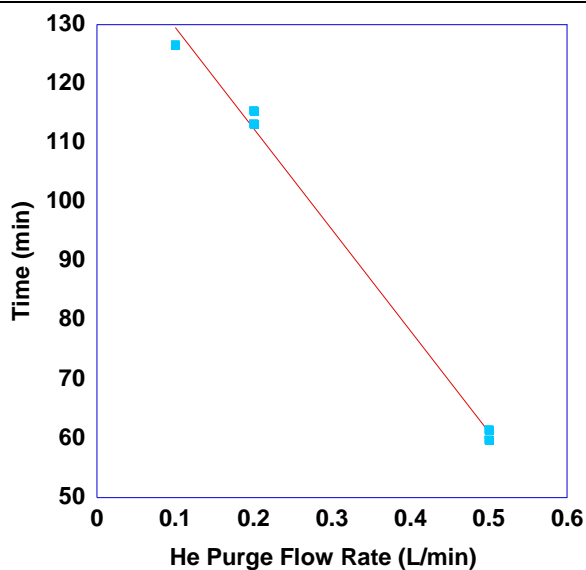
Figure 8. Deuterium residence time as a function of helium purge flow rate. The clearly linear relationship between initial breakthrough time and helium purge rate has an R^2-value of 0.961.

VI. Conclusion

Once the cryotrap was tested at full, its maximum capacity was calculated to be 5.99 sL of hydrogen, or 58.5 scc hydrogen per gram of molecular sieve. The cryotrap's crushed molecular sieve capacity can be regenerated after contacting impurities by heating the coil while simultaneously pushing a pure helium purge through the coil. A *Pd/Ag* membrane can be used to detect the pressures of hydrogen released from the cryotrap, and the cryotrap can serve as a concentrator for the loading of tritium onto uranium beds. Furthermore, the cryotrap adsorbs all hydrogen from the hydrogen-helium stream until breakthrough.

At one-fifth capacity, it was discovered that hydrogen will elute from a cold cryotrap, and there is a logarithmic relationship between the hydrogen residence time and helium purge flow rate. In addition, it was confirmed that the initial release of gas from the cryotrap is composed of deuterium molecules, and there is a linear relationship between this initial breakthrough time and the helium purge flow rate.

Before implementation, further experimentation must be conducted with deuterium and tritium to determine if the cryotrap acts in a similar manner with these isotopes.

VII. Acknowledgements

VIII. References

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