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# Validation of Hydrogen Exchange Methodology on Molecular Sieves for Tritium Removal from Contaminated Water

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# Background

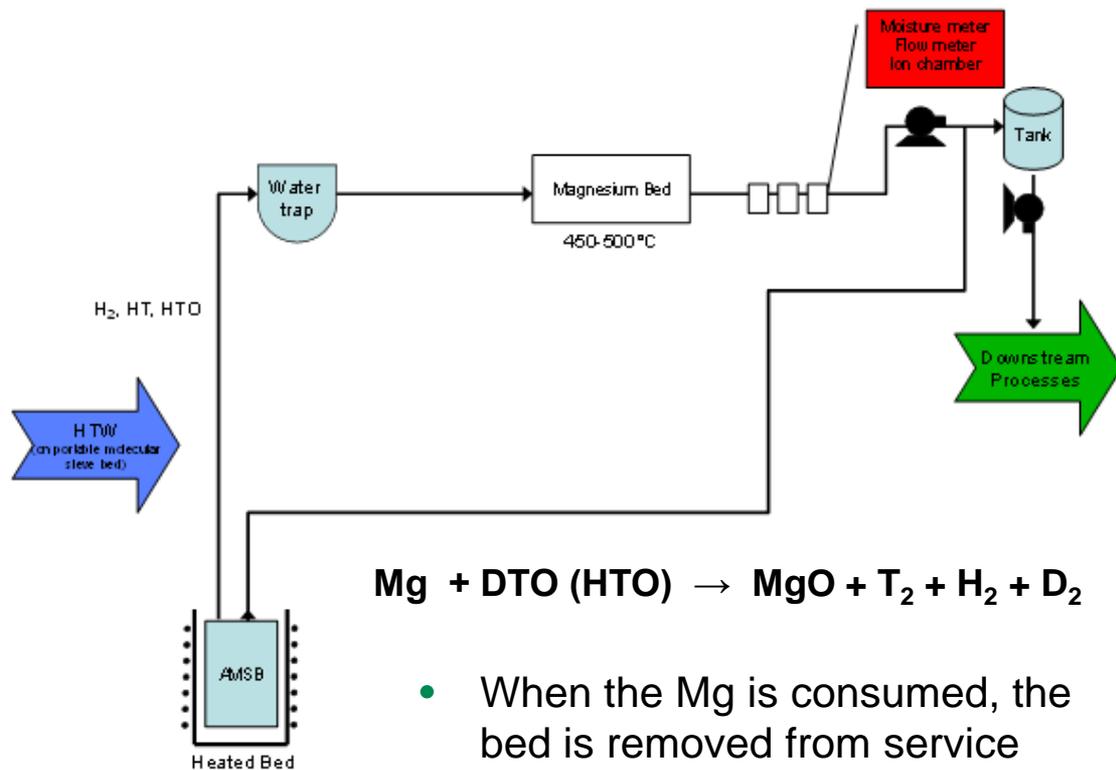
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- Tritium contaminated water is a critical issue for nuclear power reactors, especially when ground water becomes contaminated.
- Planned tritium plants for ITER and other fusion energy applications will have large volumes of tritium contaminated water – potentially highly tritiated water (~50% T).
- SRS Tritium Facility process about 200,000 liters/year of gaseous hydrogen isotopes originated from captured contaminated water.
- Hazards of Tritiated Water
  - Significantly more radiotoxic (roughly 20,000 times higher) than DT, HT, or T<sub>2</sub> gas.
  - Disintegrates through self-radiolysis into molecular hydrogen and oxygen, forming a potentially explosive mixture.
  - More corrosive than H<sub>2</sub>O due to the presence of peroxides formed during the radiolysis process.

# Driver and Benefits

## Current Method used by SRS to process tritiated water:

- Tritiated water is adsorbed on non-catalyzed molecular sieve beds.
- The beds are desorbed when completely loaded with tritiated water.
- The desorbed water is passed through a heated magnesium bed.
- Water reacts with Mg to form magnesium oxide and molecular hydrogen and tritium. The tritium is recovered and the protium is discharged.



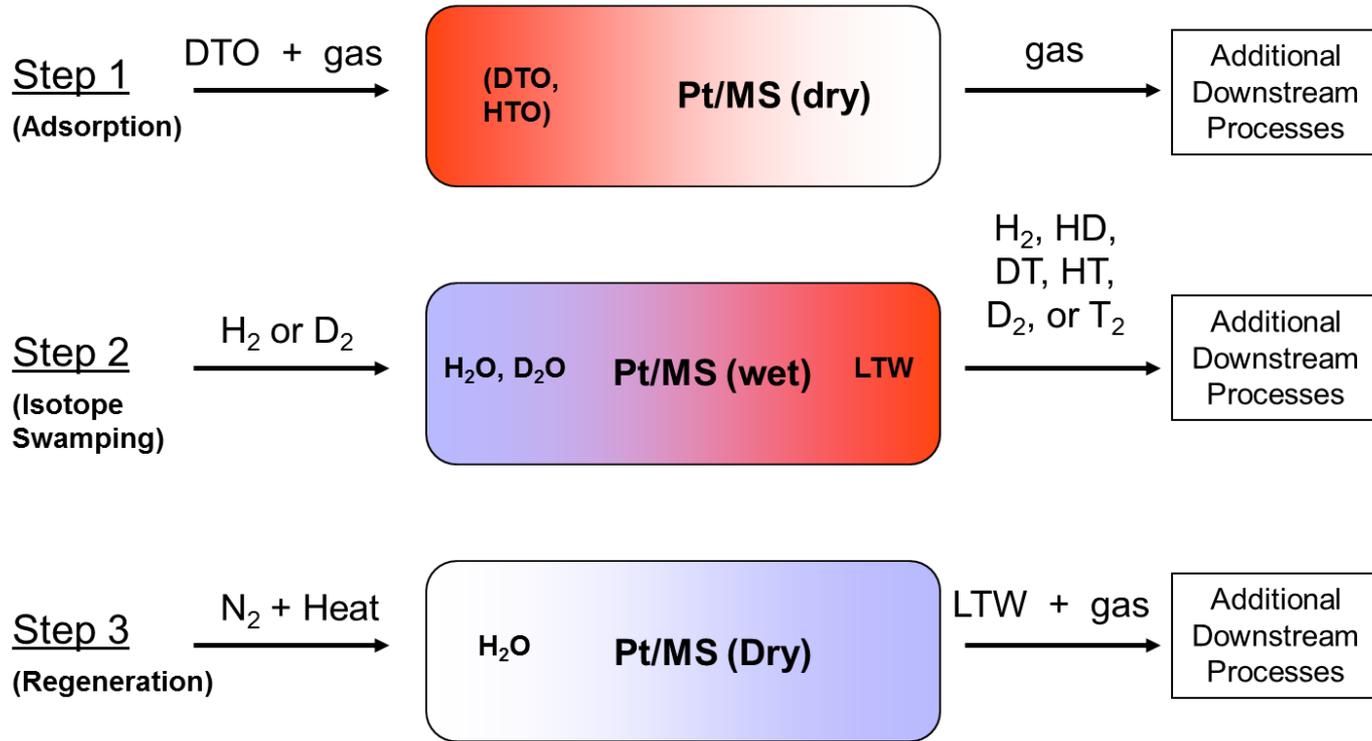
- When the Mg is consumed, the bed is removed from service and disposed of as low level radioactive waste.
  - Roughly 500 pounds each.
  - Changed out roughly once a month.
  - \$500,000 per year for the replacement of Mg beds (not including disposal cost)

## Driver and Benefits (con't)

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- **The Capture and Exchange method developed by SRNL can be implemented for the cleanup of tritium contaminated water.**
  - If the tritiated water was adsorbed on Pt-catalyzed molecular sieves initially, then the Capture and Exchange method could be used to remove the tritium, eliminating the need to transfer the tritiated water
  - This is the first step toward the elimination of the use of the Mg beds to process tritiated water. Additional water cracking techniques and the means to concentrate low levels of tritium in large quantities of water are currently being investigated. This is the necessary second step of the process to utilize the Capture and Exchange method for tritium removal.
- **Potential Applications**
  - SRS Tritium Facilities
  - Fusion Programs
  - DOE sites with tritiated water
  - Commercial Power Plants

# Capture and Exchange Method for Tritiated Water Cleanup



Step 1: Tritium contaminated water is adsorbed on Pt-catalyzed molecular sieves.

Step 2: An excess of deuterium is flowed through the molecular sieves at room temperature. The deuterium will exchange with the tritium in the sample leaving the deuterated water (D<sub>2</sub>O) on the surface.

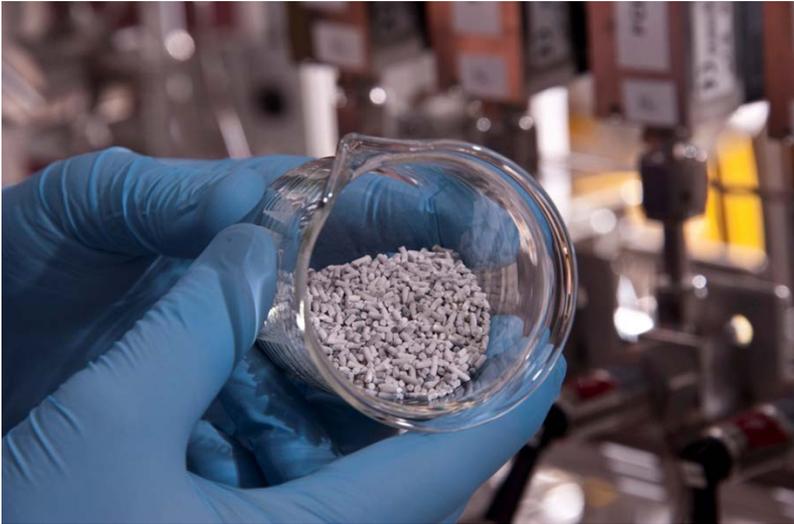


# Experimental Approach

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- **Material Preparation**

- Pt-Deposition Method – Pt is deposited on the surface of the molecular sieve material (Y-type Zeolite).
  - Material mixed with binder and support agents, extruded and then mixed with Pt catalyst
- Pt Ion-Exchange Method – Pt ions exchange with  $\text{Na}^+$  ions in the molecular sieve (Y-type Zeolite) and become part of the structure.
  - Mixed with catalyst and then with binder and support agents and then extruded
- Samples were catalyzed at 1.0%, 1.5% and 2.0% Pt



# Experimental Apparatus

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- Pressure transducers
- MKS Flow Controllers
- Gas supplies of Ar, N<sub>2</sub>, and H<sub>2</sub>
- 2 Residual Gas Analyzers
- 1 Inficon micro GC
- Flow through testing

- 3/4" Stainless Steel Tubing  
6" long
- VCR #12 fittings
- 0.5 micron stainless steel  
fritted VCR Gaskets
- Horizontal configuration
- Clam-shell style heaters

- Inficon 3000 micro GC
- Dual identical molecular  
sieve columns
- 60°C column, sample  
injector, and sample inlet  
temperature



# Experimental Parameters

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## Drying Regimen

- Roughly 20 grams of Pt-catalyzed molecular sieve materials were loaded into a double ended test cell for flow through testing.
- Flow 2L/min N<sub>2</sub> through the molecular sieves
- Heat to 350°C for 48-72 hours until dewpoint is ~-40°C

## D<sub>2</sub>O Loading Regimen

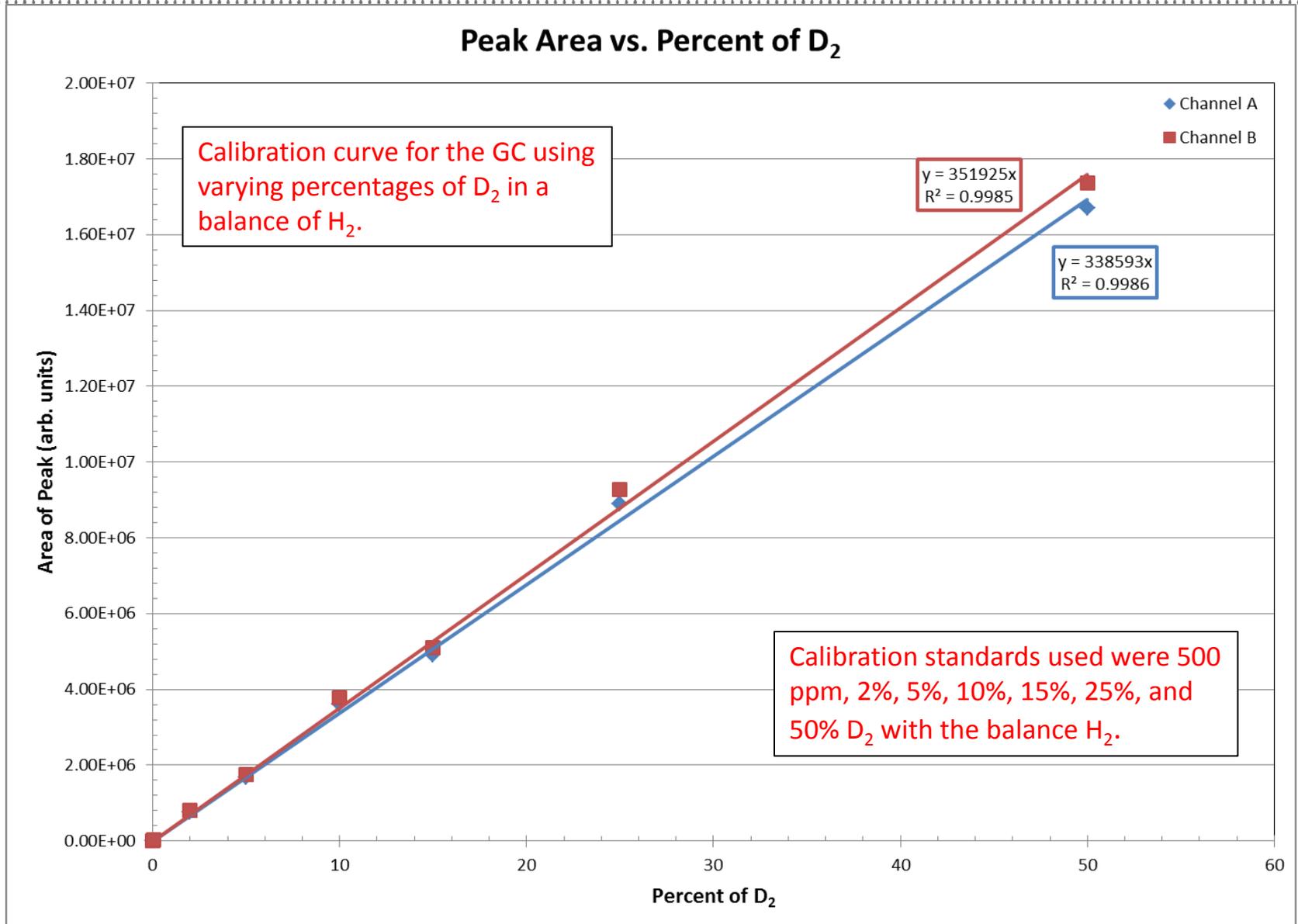
- 15% by weight D<sub>2</sub>O is loaded into the D<sub>2</sub>O transfer cell
- Flow 7.25 ccm/min Ar through the deuterated water for 4.5 hours
- Heat to test cell and transfer lines to 120°C
- Molecular sieves are at room temperature and pressure

## H<sub>2</sub> Exchange Regimen

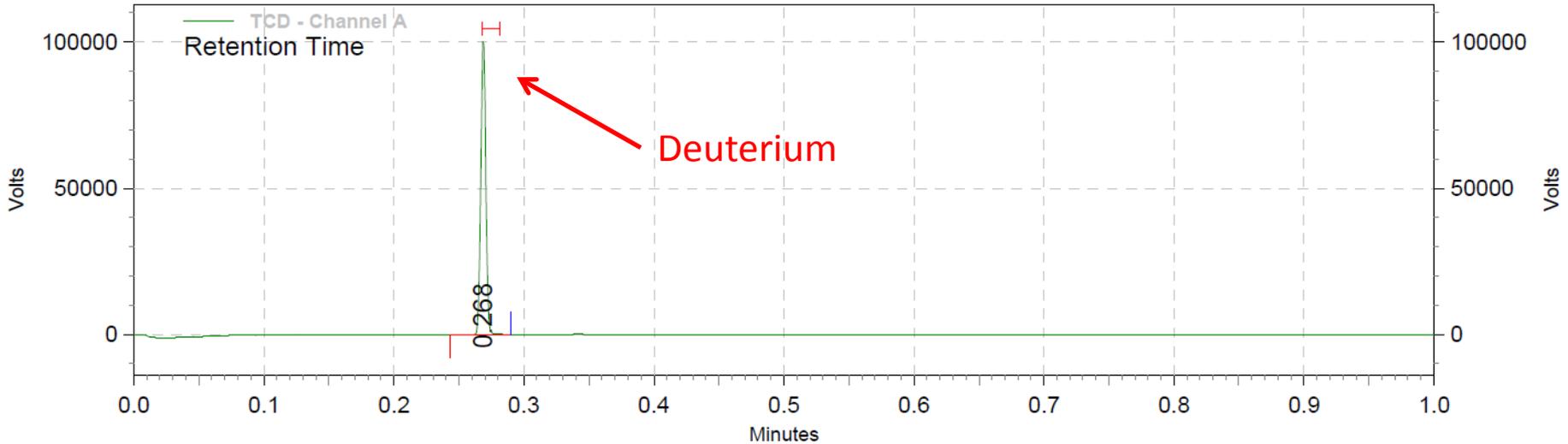
- Flow 50 ccm/min H<sub>2</sub> through the molecular sieves
- Molecular sieves are at room temperature and pressure
- Monitor exhaust stream with micro GC and RGA.



# Experimental Results



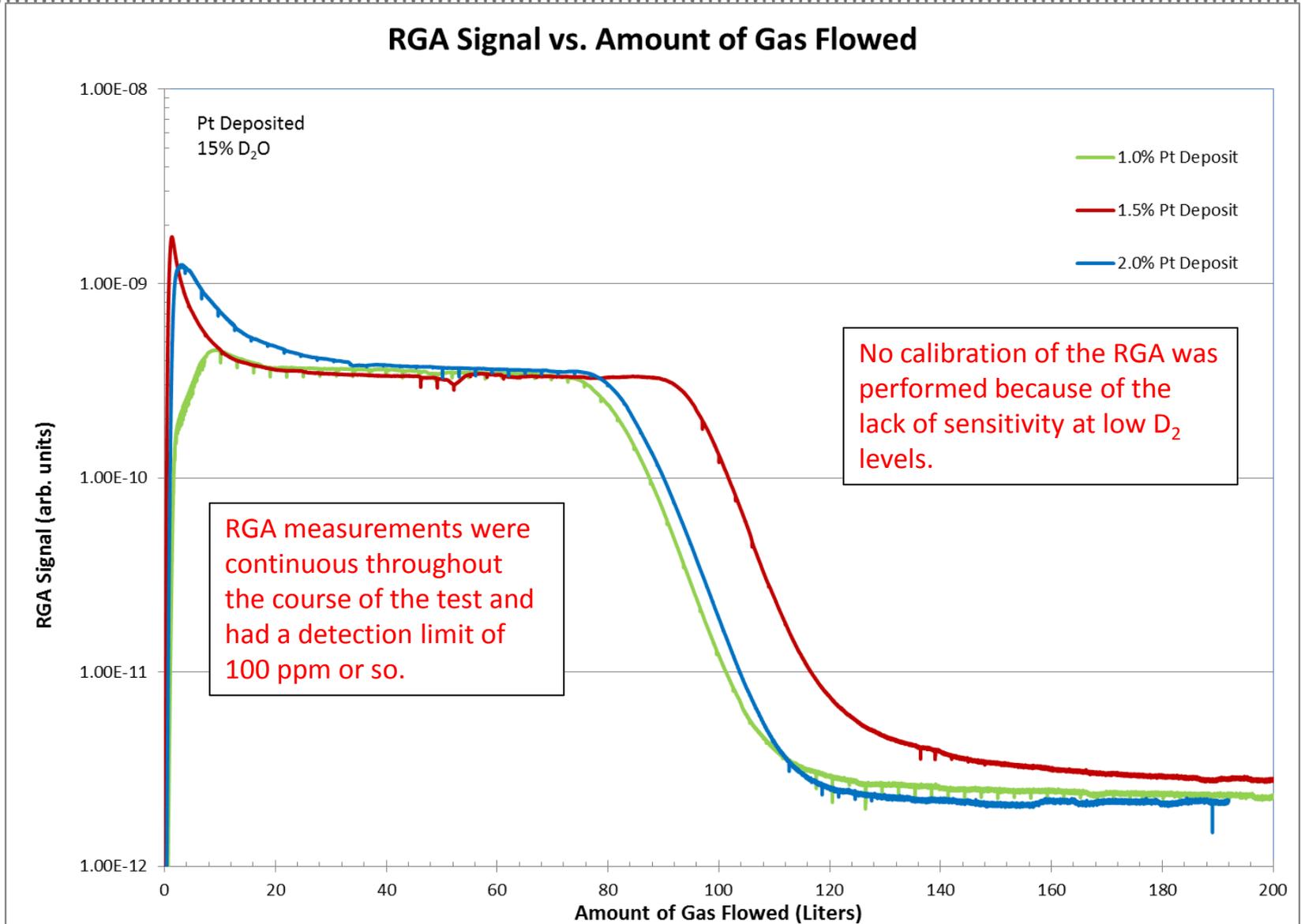
# Typical Gas Chromatogram



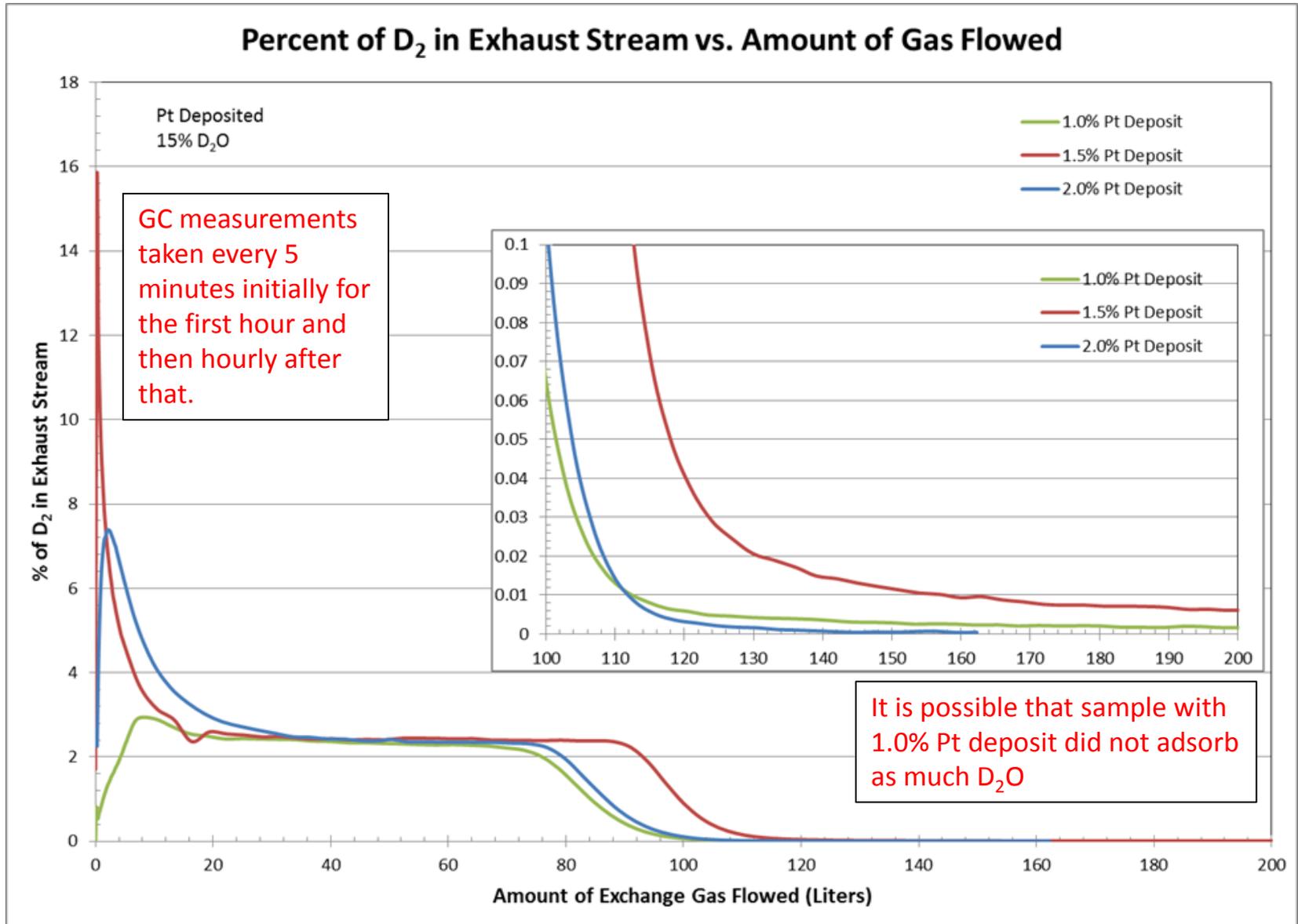
- Hydrogen is used as the carrier gas as well as the exchange gas
- Single peak in the spectra is associated with Deuterium
- Retention time for column A is 0.268 minutes and Retention time for column B is 0.223 minutes
- Detection limit down to ppm levels



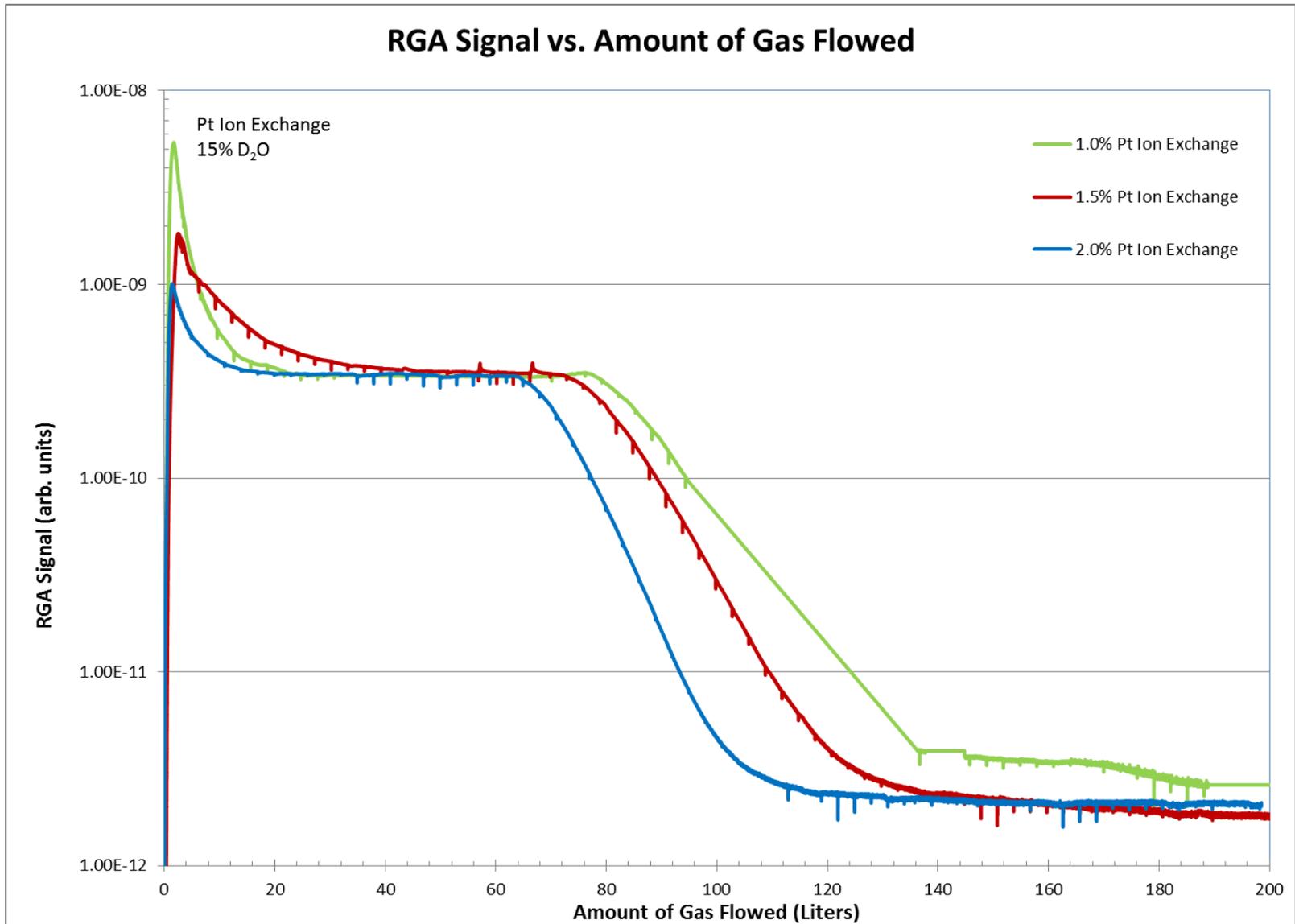
# Experimental Results



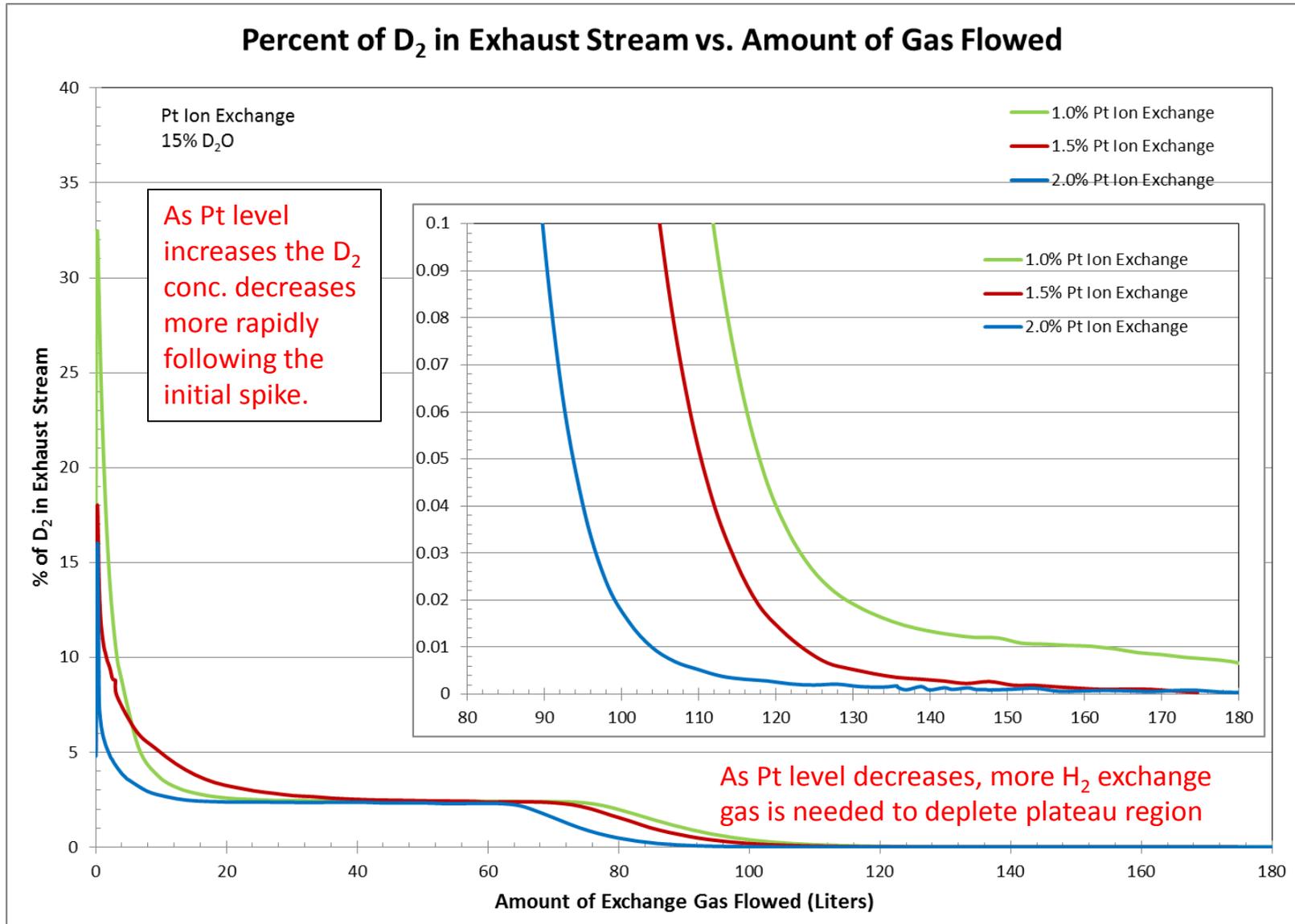
# Experimental Results



# Experimental Results



# Experimental Results



# Experimental Results - Summary

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Summary of Hydrogen Isotope Exchange Performance

Sample	Amount of H <sub>2</sub> Exchange gas to get below 1000 ppm D <sub>2</sub>	Concentration of D <sub>2</sub> after 100 L of H <sub>2</sub> exchange gas	Concentration of D <sub>2</sub> after 150 L of H <sub>2</sub> exchange gas
1.0% Pt Deposit	97 L	699 ppm	28 ppm
1.5% Pt Deposit	110 L	8993 ppm	113 ppm
2.0% Pt Deposit	100 L	912 ppm	5 ppm
1.0% Pt Ion Exchange	112 L	3709 ppm	108 ppm
1.5% Pt Ion Exchange Trial #1	121 L	5180 ppm	n/a
1.5% Pt Ion Exchange Trial #2	106 L	1945 ppm	19 ppm
2.0% Pt Ion Exchange	89 L	155 ppm	10 ppm

- Sample that show optimal hydrogen isotope exchange performance is the 2.0% Pt Ion Exchange sample
- Second best sample for hydrogen isotope exchange is 2.0% Pt deposit

# Experimental Challenges

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- An assumption was made that all the deuterated water in the test cell was loaded onto the molecular sieves.
- Even though the Ar was flowed through the D<sub>2</sub>O at 7.25 sccm, some of the water may not have adsorbed on the molecular sieves. A residence time of 4 minutes may not be long enough for all of the D<sub>2</sub>O in the Ar stream to be adsorbed on the molecular sieves
- Not possible to determine the actual water loading on the molecular sieves.
- Dewpoint of the humidified Ar was ~-20°C, compared to -40°C for dry Ar indicating that some of the D<sub>2</sub>O was not adsorbing on the molecular sieves, but we were not able to quantify the amount in the exhaust stream
- RGA signal was inconclusive due to overlapping signals from Ar for mass 20

# Summary and Conclusions

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- A total of 6 Pt-catalyzed molecular sieve samples have been prepared using the Pt-deposition and Pt-Ion Exchange method.
- Samples were catalyzed with Pt at 1.0%, 1.5%, and 2.0% Pt
- The hydrogen isotope exchange efficiency of each sample was determined by flowing H<sub>2</sub> through a D<sub>2</sub>O loaded sample.
- The sample that was catalyzed with 2.0% Pt using the ion exchange method appears to be the best overall sample and exhibits the best hydrogen isotope exchange efficiency. 89L of H<sub>2</sub> exchange gas were needed to reduce the D<sub>2</sub> concentration to below 1000 ppm.
- The hydrogen isotope exchange is the most efficient when large amounts of D<sub>2</sub>O are adsorbed on the molecular sieves. As the amount of D<sub>2</sub>O decreases on the surface the hydrogen isotope exchange efficiency decreases.
- The Capture and Exchange method would be effective at removing the tritium from contaminated water, but would need to be used in collaboration with a method that could concentrate the tritium in the water to reduce the volume.

# Future Work

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- Phase 2 of this work has been funded through the NNSA Nuclear Safety Research and Development Working Group.
- In Phase 2, several of the Pt-MS materials that exhibited the best hydrogen isotope exchange performance will be selected for testing with tritiated water
  - The two samples with 2.0% Pt catalyst (Ion-Exchange and Pt-Deposition)
  - 1.5% Pt using the Pt-Ion Exchange method
- In order to complete the tritiated water testing, a collaboration with Pacific Northwest National Laboratory or as a second choice Karlsruhe Institute of Technology is essential
- Testing will be identical to the D<sub>2</sub>O and H<sub>2</sub> testing that has been completed in Phase 1
- The testing with T<sub>2</sub>O is necessary to confirm that the T<sub>2</sub> will not have any deleterious effects on the Pt-catalyzed molecular sieve material.
- Additional “cold” testing will also be performed on the selected samples to optimize the flow rate of the D<sub>2</sub>O loading and the H<sub>2</sub> exchange.

# Acknowledgements

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Thank You For Your Attention!