SRNL™
SAVANNAH RIVER NATIONAL LABORATORY
Operated by Savannah River Nuclear Solutions, LLC

We Put Science To Work

Tritium Instrument Demonstration Station (TIDS)

Laura Tovo

September 24, 2014

Tritium Focus Group Meeting

SRNS-STI-2014-00423

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Plant Directed R&D PDRD

What is the challenge?

Tritium Facilities is critically reliant on dated analytical technologies

Low-mass, high-resolution mass spectrometer issues:

- Near end-of-life (30+ years old)
- Spare parts not available from vendor
- Vendor support is difficult or unavailable

Lifetime extended through SRNL R&DE developed:

- Intensive electronic upgrades
- Hardware modifications

Need for alternative, accessible analytical technologies within DP for:

- Complement current analytical methods
- Greater ability to troubleshoot process issues
- Minimization of process upsets and delays
- Optimization of process performance

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Purpose of the PDRD – TIDS FY14

PDRD Fulfillment SRS Tritium Mission – Key Work Scope:

- Maintain skill set and core competencies related to Tritium Facilities
- Integrate SRNL research with Tritium Facility objectives and needs

FY14 Goals:

1. Operation of TIDS in P1 glovebox in 233-H
2. Verification of calibrations using H and D species.
3. Calibration of instrumentation with tritiated species.
4. Analysis of Process sample.

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What measurements are important for Tritium Facilities?

System	Sampling Location	Species
TPS	Inlet TPS/ Outlet ST-909	NX_3, CX_4, X_2O
HT-TCAP	Col C PCV	X_2, N_2, X_2O, CX_4, He
ZR	Tank	NX_3, CX_4, X_2O
Stripper/ ZR	Glovebox	X_2O, NX_3, O_2, sulfurs, hydrocarbons, CO_2, CO
TCAP/ HT-TCAP/ P-Evac	Feed/ Recovery Beds/ Product & Feed headers	X_2, N_2, He, X_2O
DI	Inlet/ Outlet of: FTB, DE, Diffuser Stage, Downstream from ST-198	N_2, NX_3
DI/P-Evac	DE Vessel/ Acc. Tank	NX_3, X_2O, X_2
SCLU	Possibly around the 100L tank	CX_4
Mixing	Ar and D_2 cylinders	Ar, X_2, O_2

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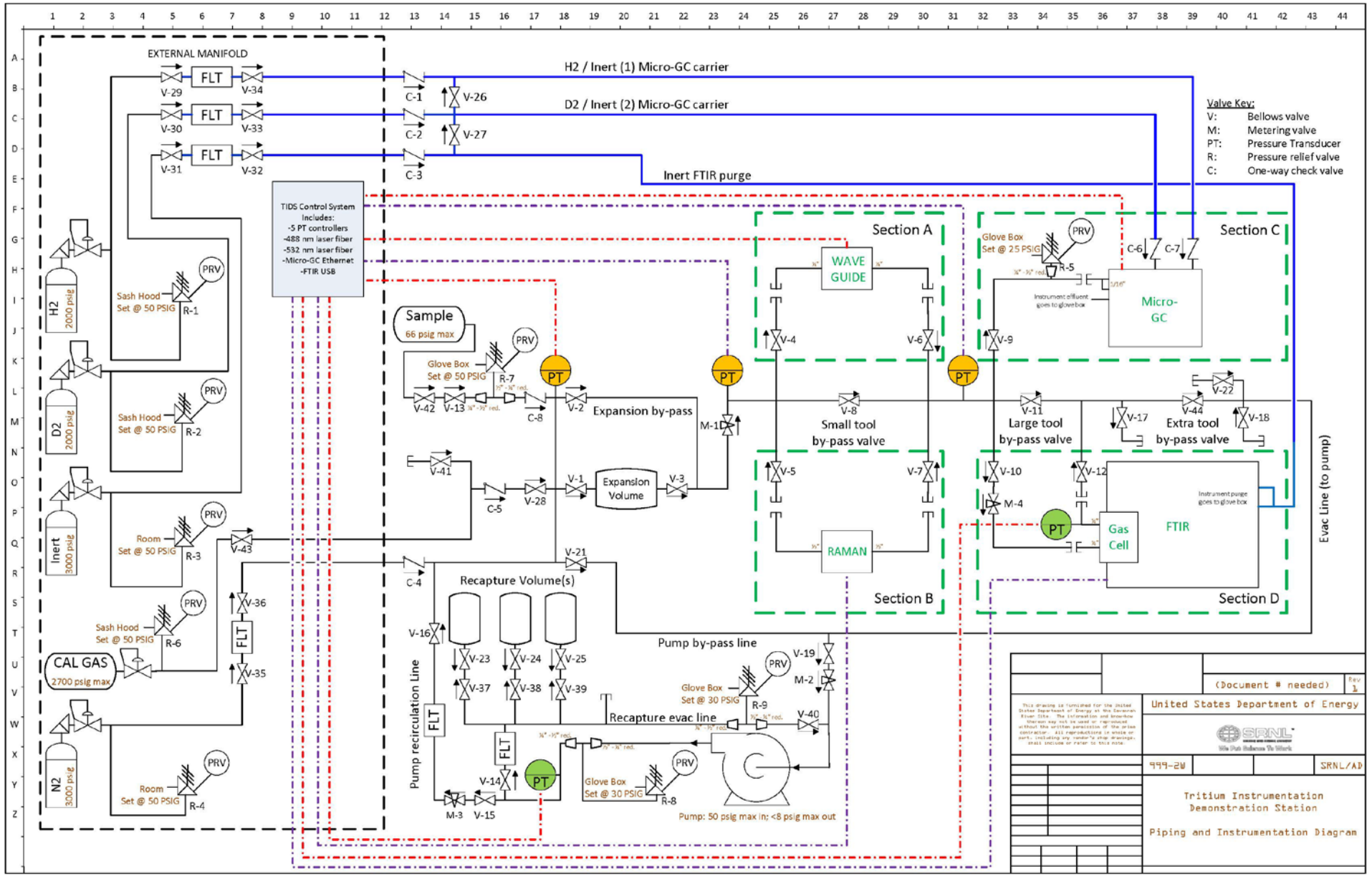

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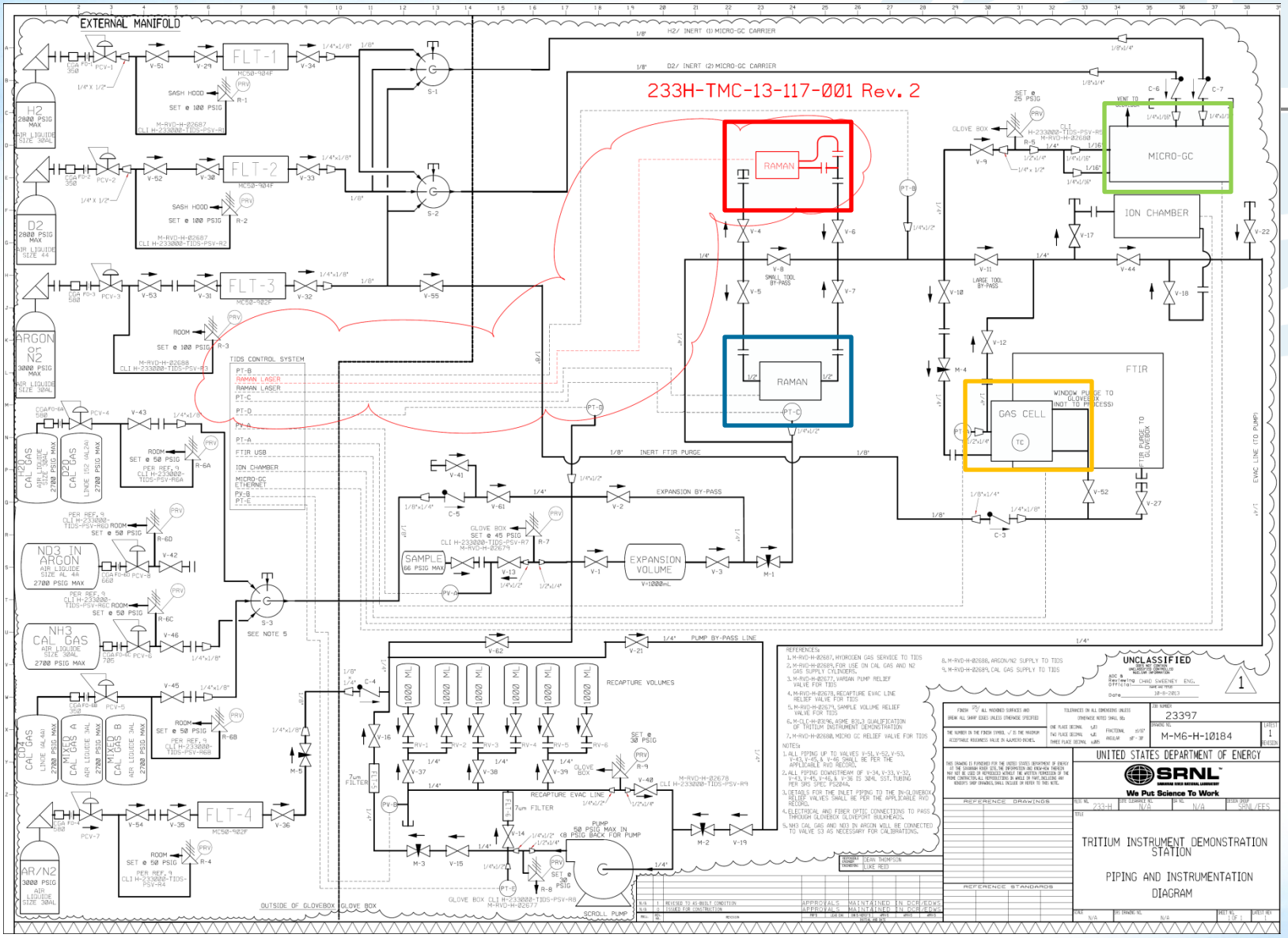

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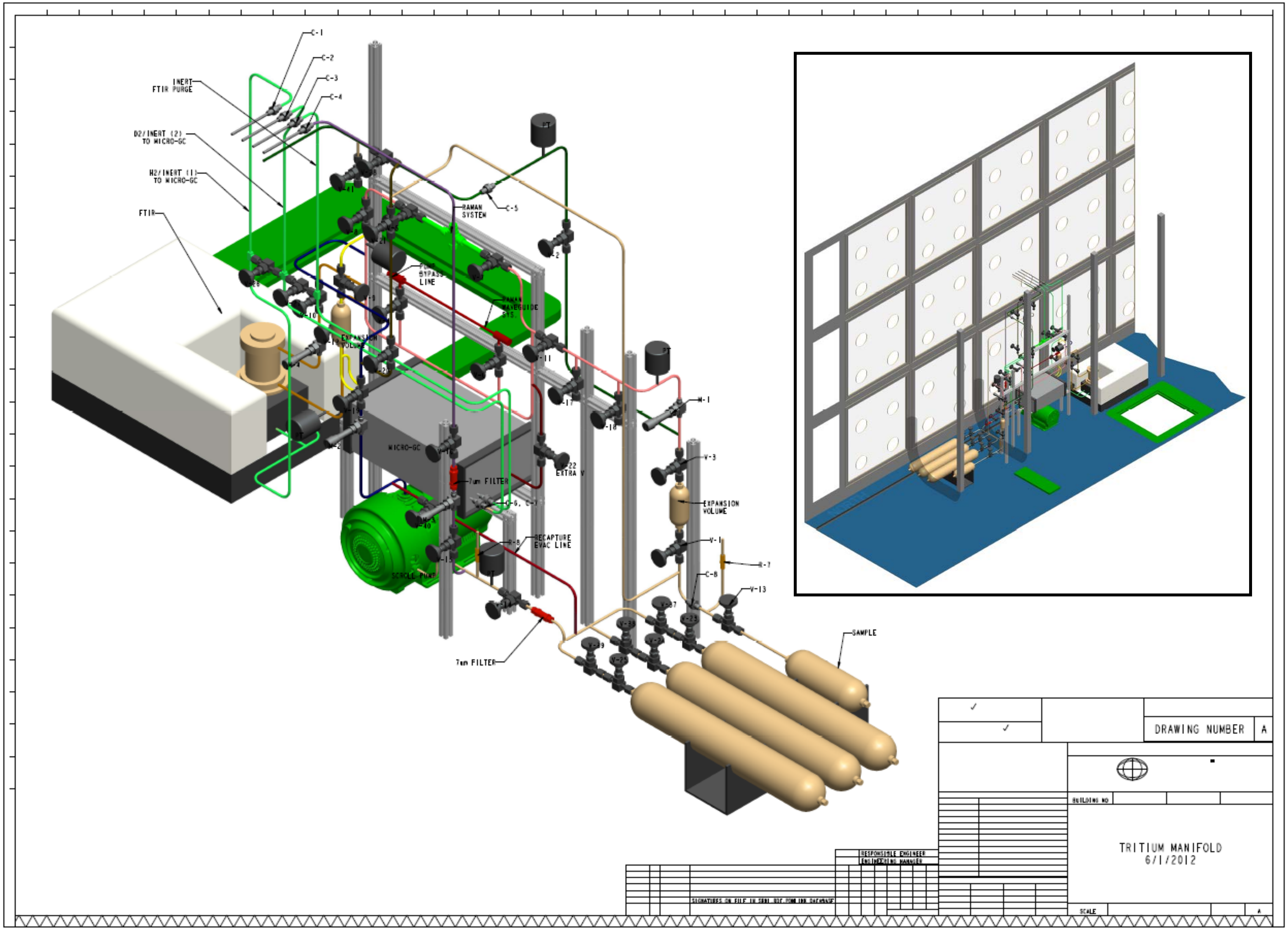

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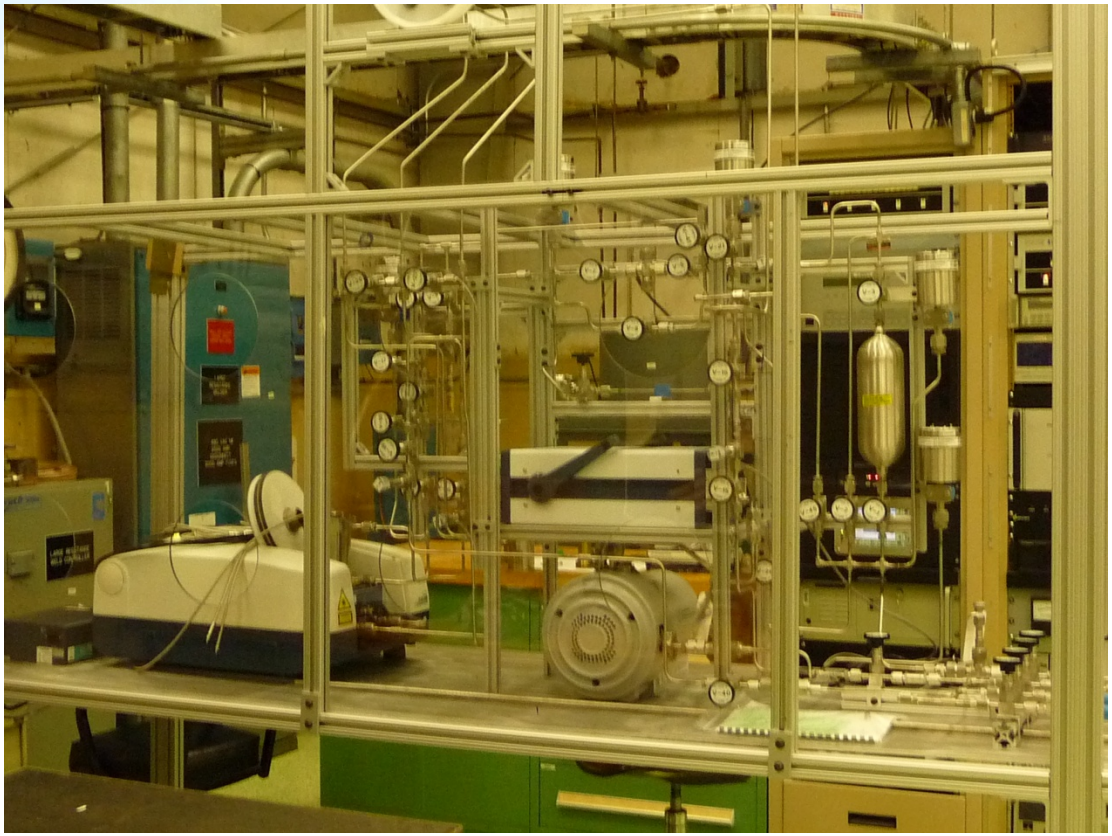
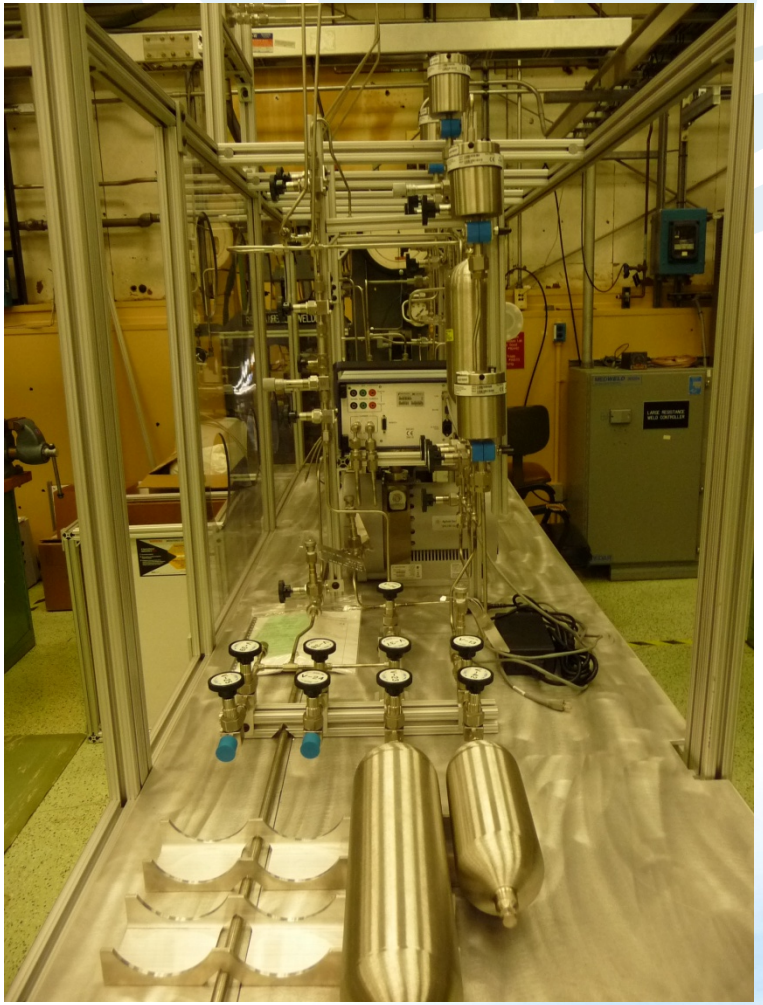
From sketch to finished product – TIDS fabrication





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Analytical Instrumentation Specs

A) Fourier Transform Infrared Spectrometer (FTIR)

Tool:

JASCO 4200

CIC Photonics 4Runner (6 meter) custom-made gas cell

Detection Purpose:

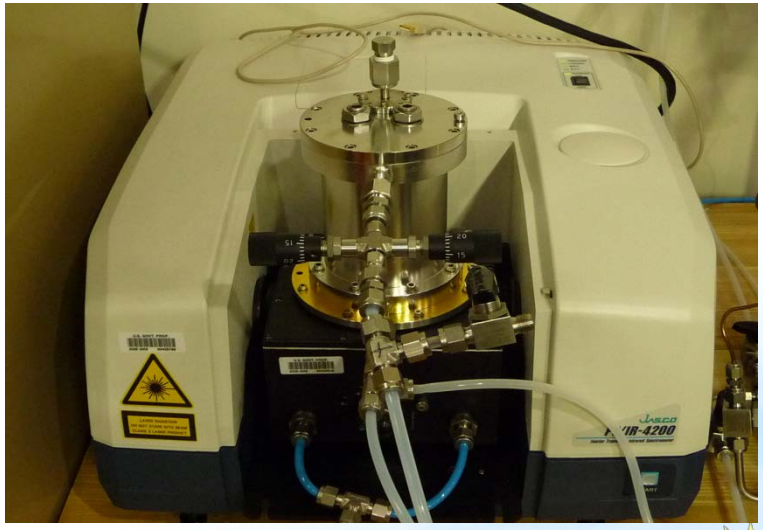
NX_3, CX_4, X_2O, CO_2, CO, C1 to C4 analytes

Sensitivity / Limit of Detection (LOD):

<1 ppm with appropriate gas cell

Uncertainty:

5% at ~ 1ppm



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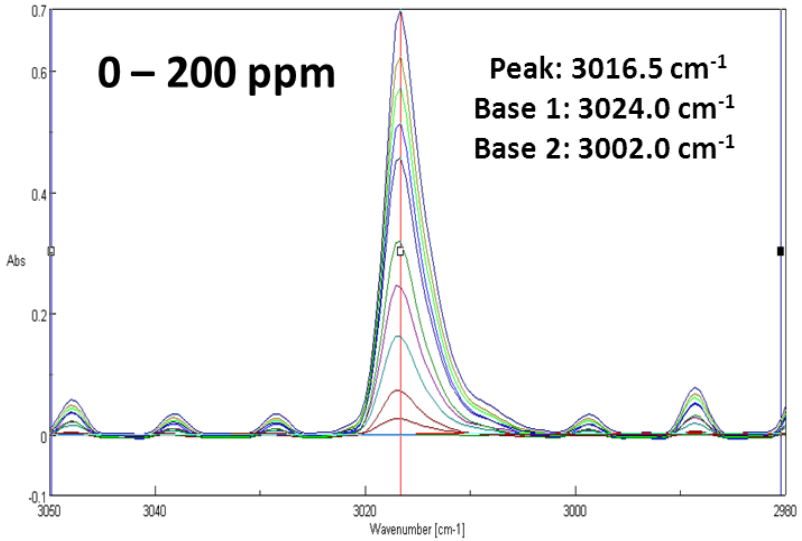
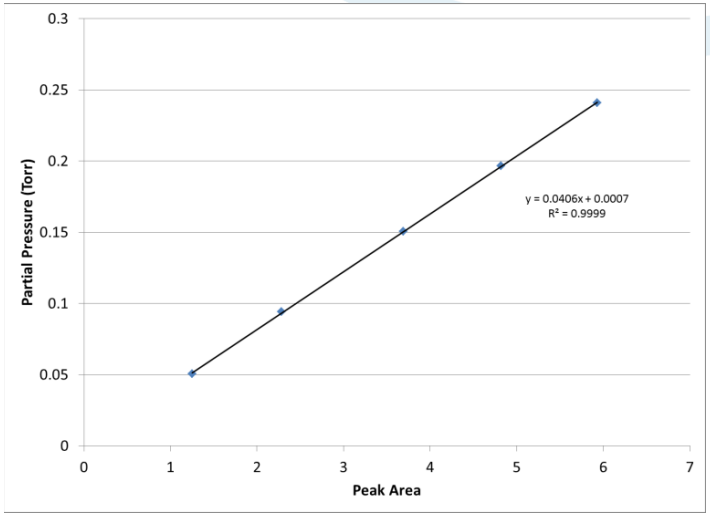
Sample FTIR Spectra: CH_4

Asymmetric C-H stretching





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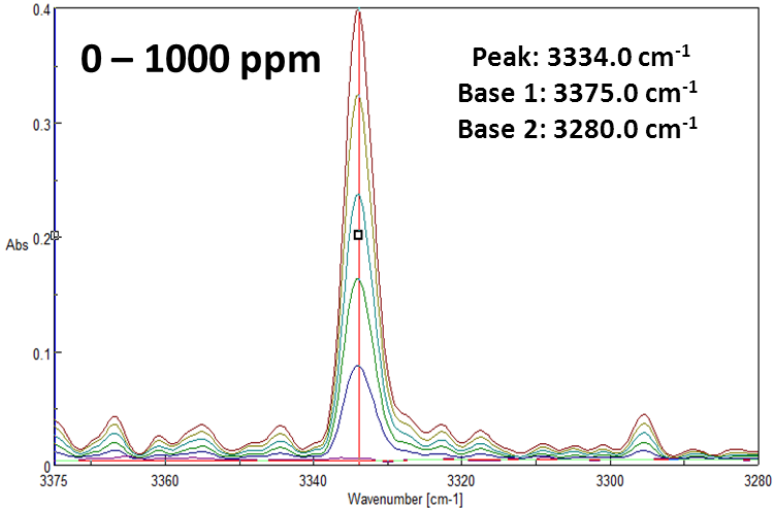
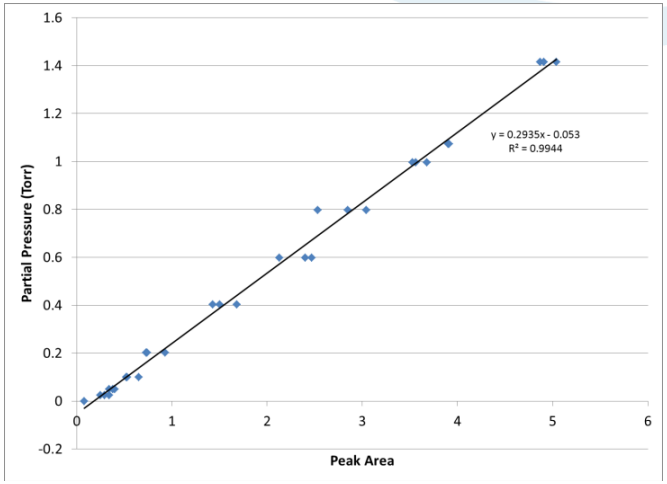
Sample FTIR Spectra: NH_3

Symmetric N-H stretching





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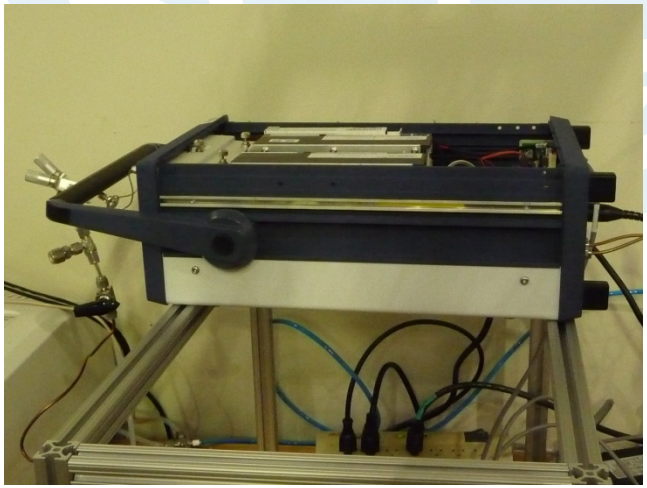
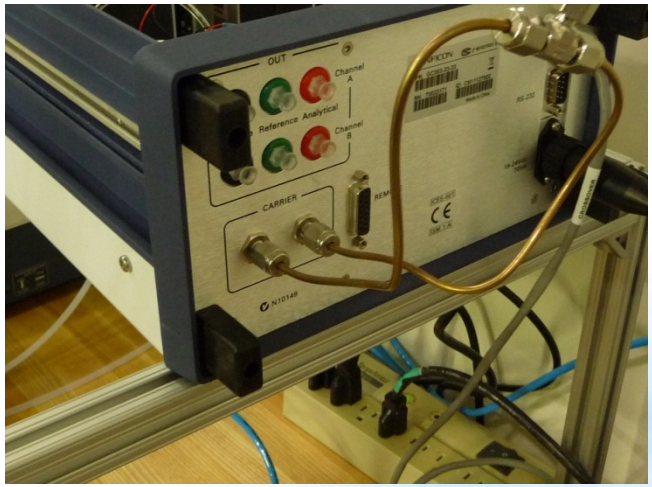
Analytical Instrumentation Specs

B) Micro Gas Chromatography (Micro GC)





Tool:

Inficon (Agilent) 3000 Micro GC

Duel 5A mol-sieve PLOT columns (10 m)

Plot U (6 m) on order

Detection Purpose:

X_2, CX_4, CO_2, N_2, He, CO

NX_3

Sensitivity / Limit of Detection (LOD):

~200 ppm for “X” isotopologues

~10 ppm for all non-X analytes

Uncertainty:

3-5% typical

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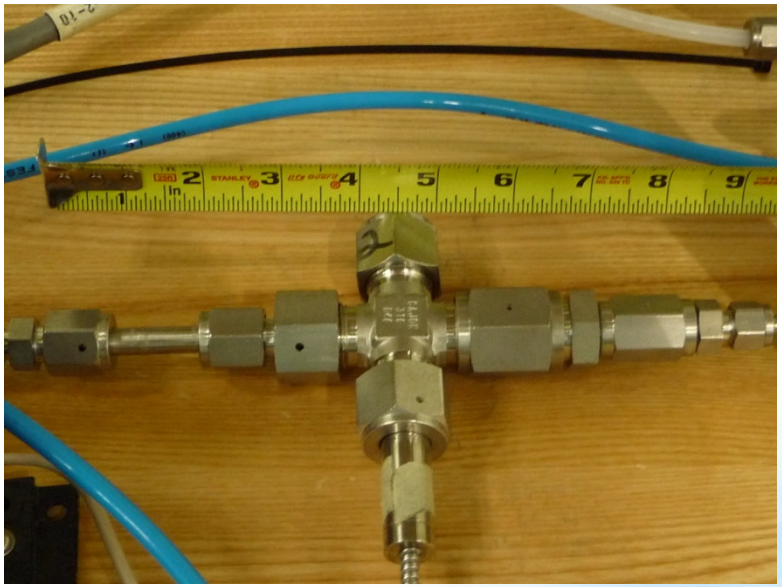
Analytical Instrumentation Specs

C) SRNL-developed Raman probe

Tool:

Coherent Sapphire 200 – 488 nm; 200 mW max power
RoMack Inc. 20' fiber optic (6 around 1) on ½" VCR fitting
Kaiser Optical Holospec- f/1.8 I VIS w/ 488 grating
Andor DV-420-OE CCD detector



Detection Purpose:

Primary – X_2, CX_4, N_2
Secondary – NX_3, CO_2, CO

Sensitivity / Limit of Detection (LOD):

> 1000 ppm for X_2
Unknown for other analytes

Uncertainty:

2-5% typical

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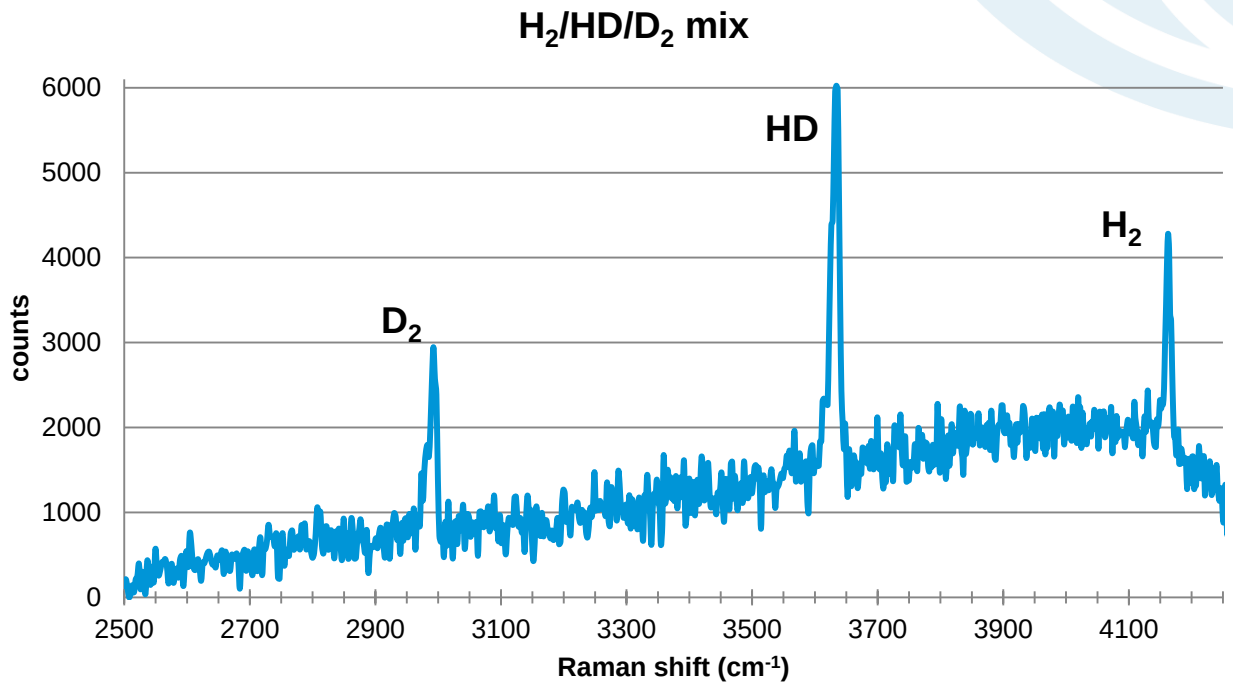
Sample Raman Spectrum



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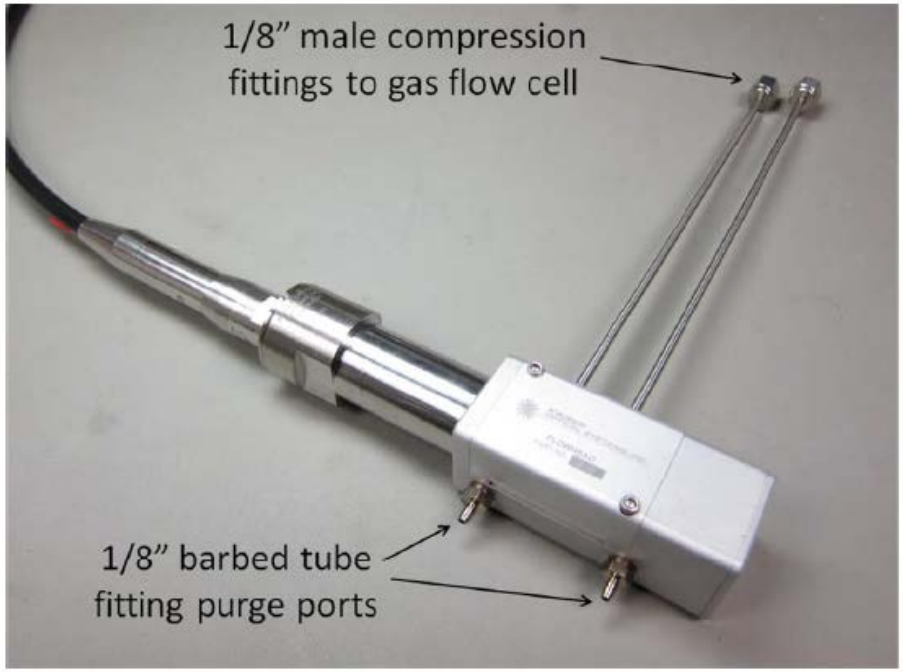
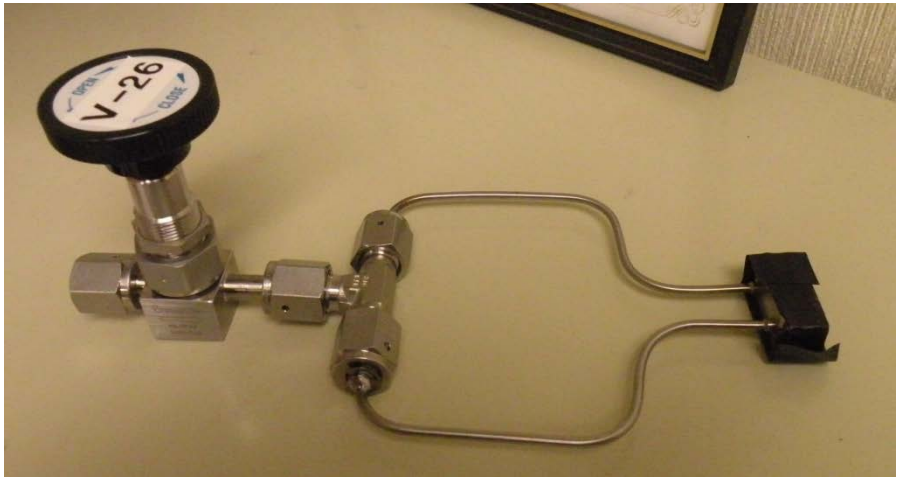
Raman Probe

- **Kaiser “AirHead” probe with “FlowHead” attachment**
  - Gas cell inserted into retroreflection cavity
  - Cell is part of manifold; reduces demands on fiber integrity





FlowHead before insertion into probe

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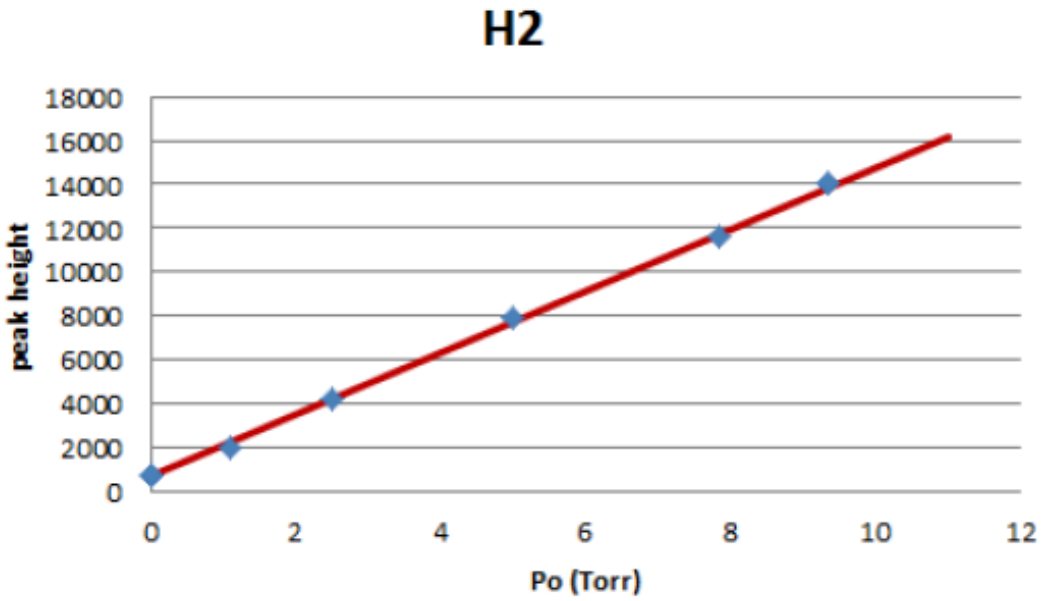
Raman Probe – lab results with FlowHead

- **Estimated LODs:**
  - H_2, $D_{2:}$ ~0.2-0.3 Torr
  - (~300 ppm for 1 atm sample)
  - CH_4: 0.1 Torr
  - CO_2: 0.4 Torr
  - O_2: 1 Torr
  - N_2: 2 Torr



- **Probe/method status:**
  - Probe installed in glove box and functional
  - Optimization of gas cell position required to increase signal
    - (decrease time required to obtain above LODs)

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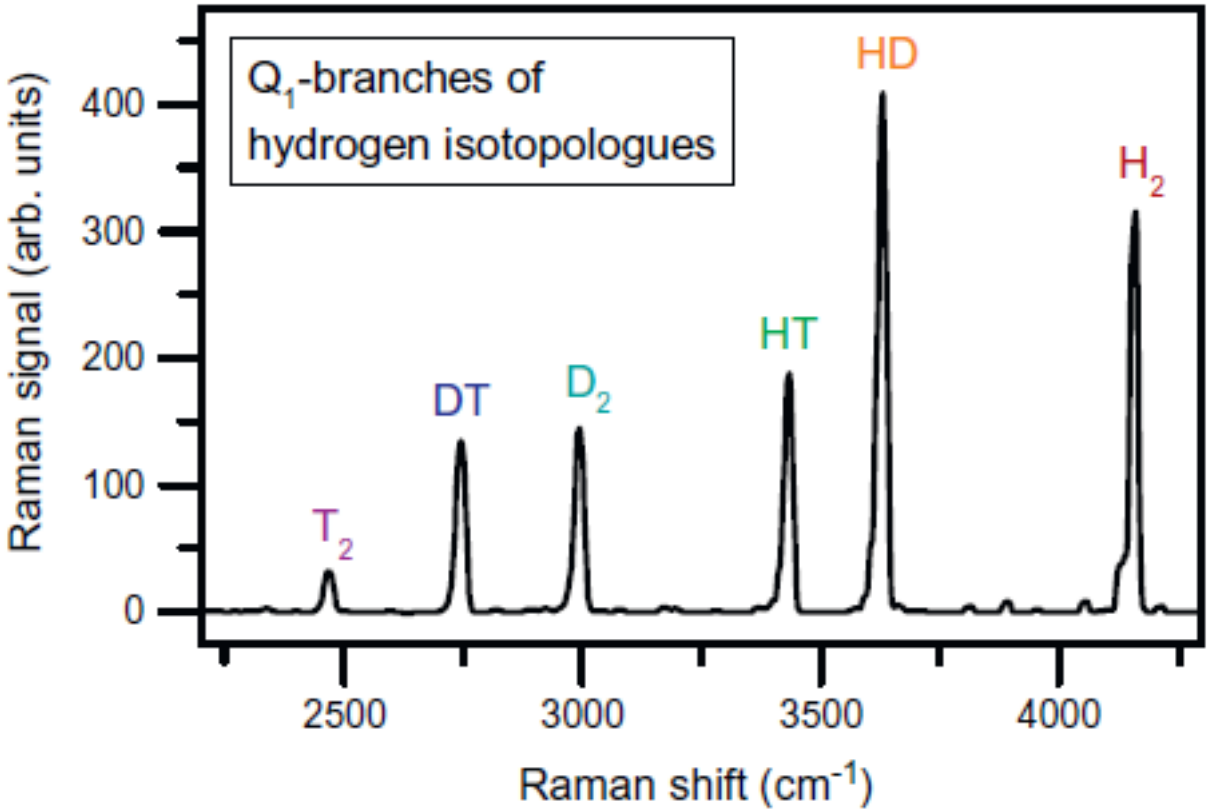
Raman Spectrum of X_2 isotopologues



from M. Schlösser *et al. J. Mol. Structure* 1044 (2013) 61.

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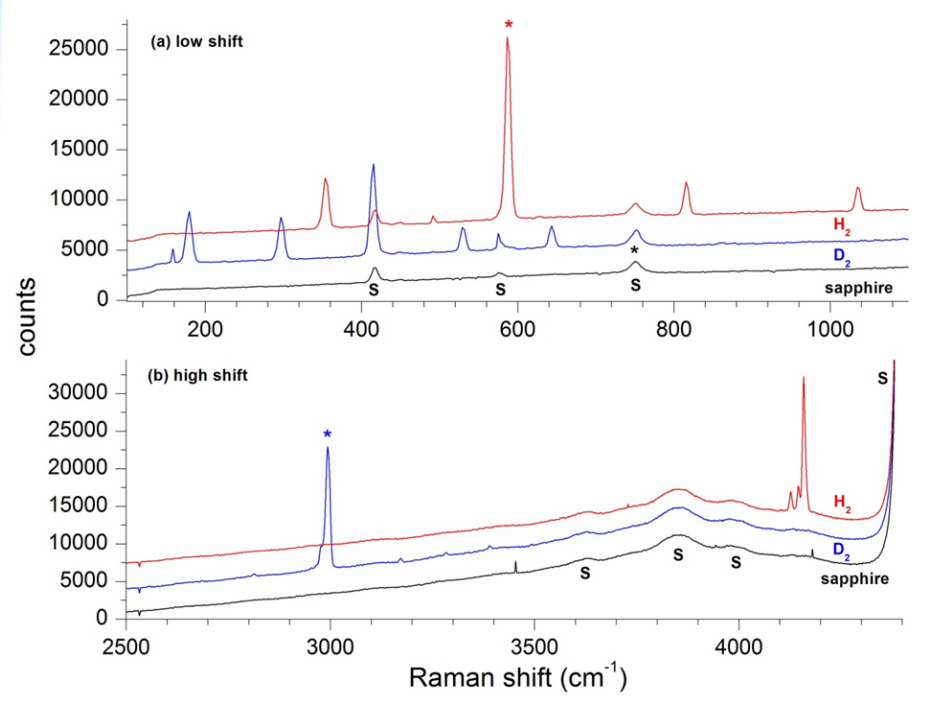
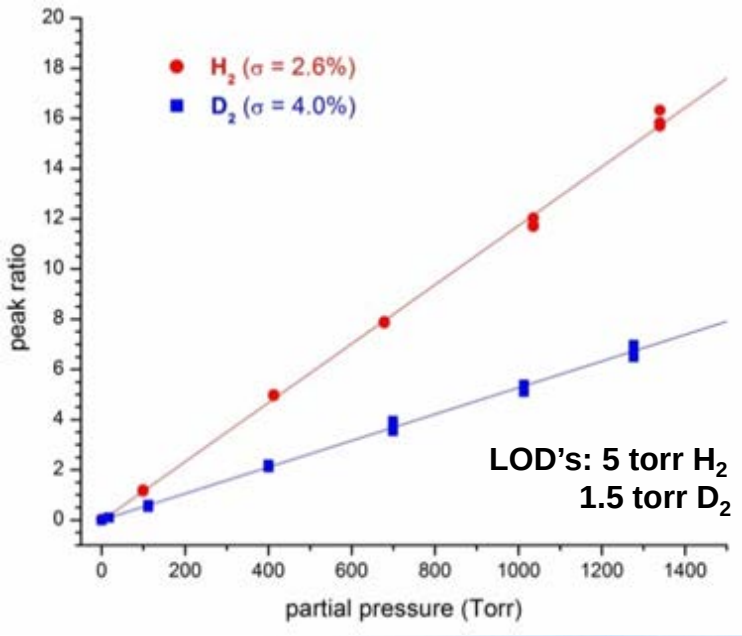
Raman-H_2/D_2 spectra



H_2/D_2 Calibration



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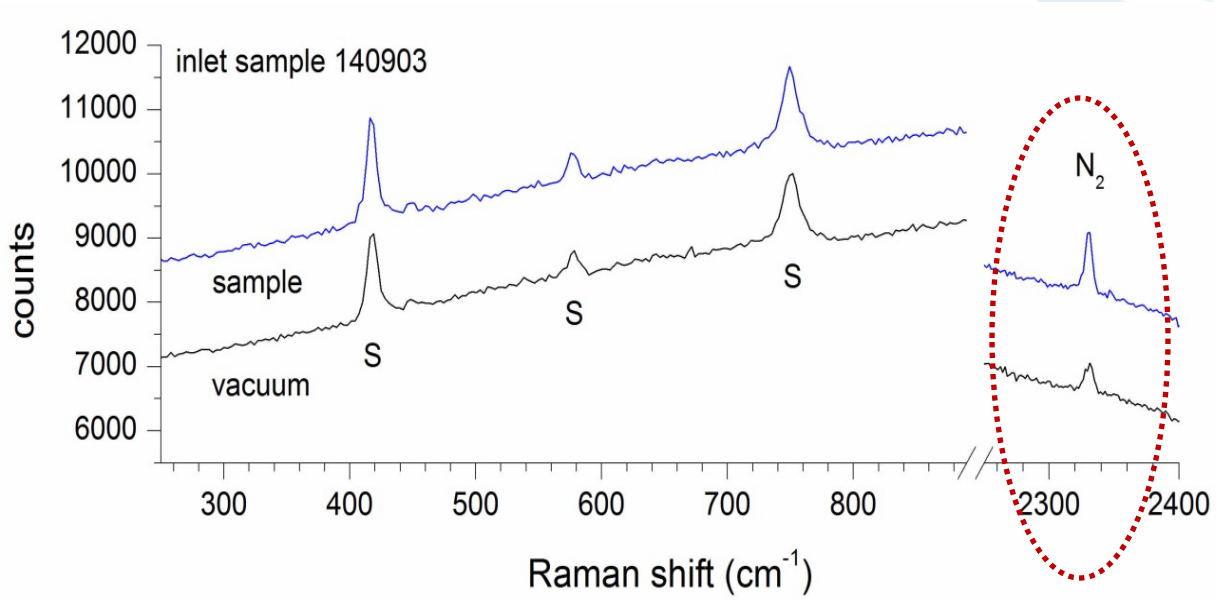
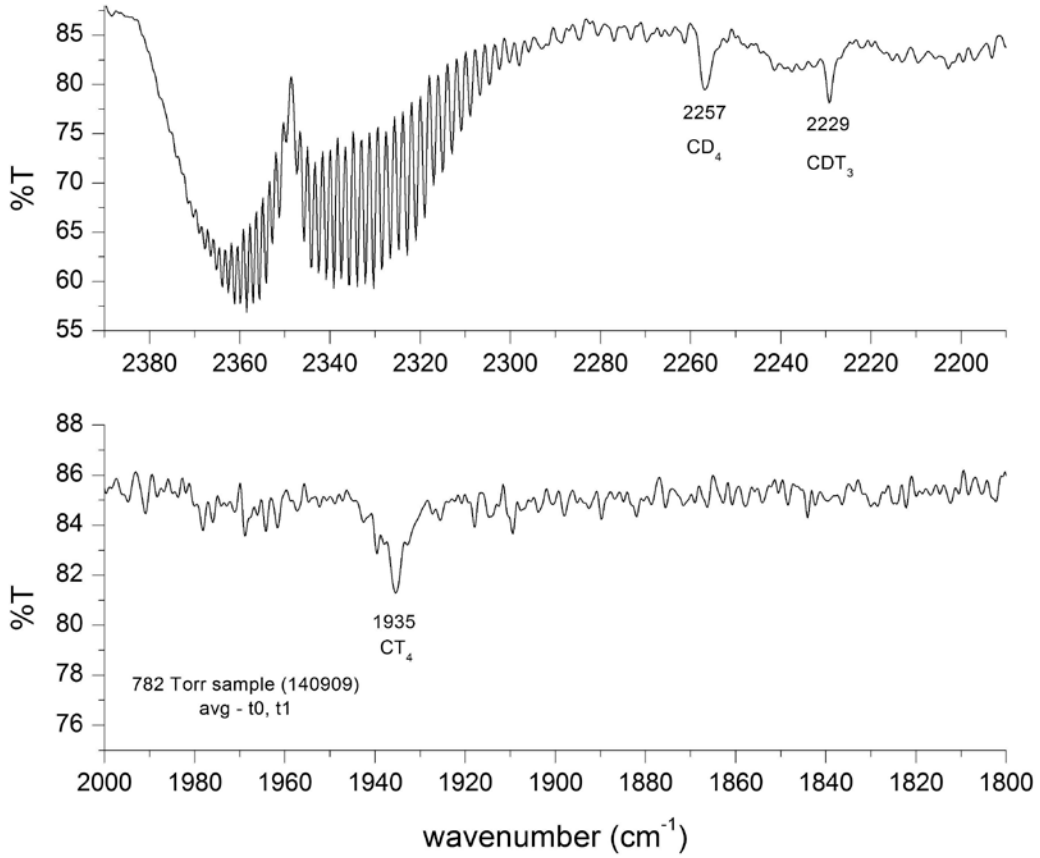
Sample Analysis

Raman spectra



Sample Analysis

FTIR spectra



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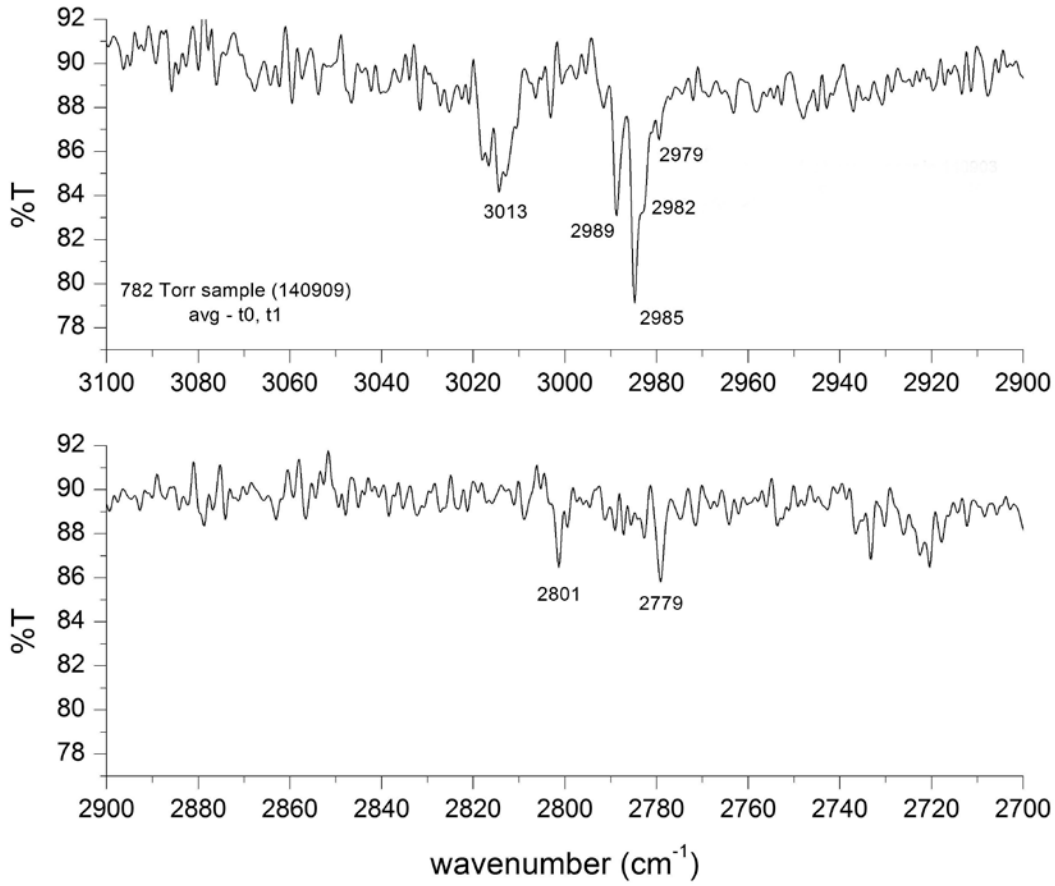
Sample Analysis

FTIR spectra



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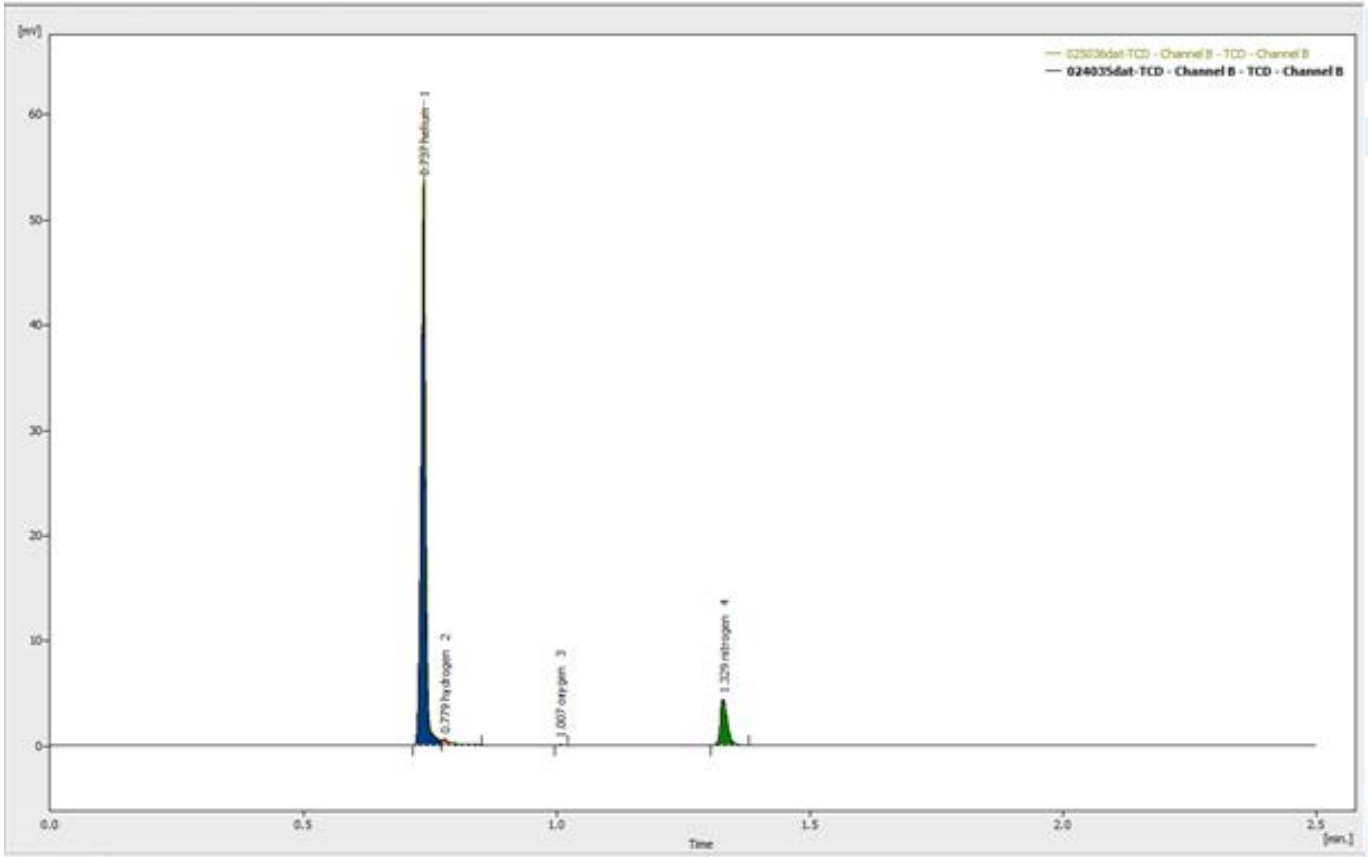
Sample Analysis

Gas chromatogram



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Quantitative Results

ID	Sample #1 Concentration (ppm)	Sample #2 Concentration (ppm)	Analytical Instrument
N_2	85,000	76,000	Raman
CO	28	22	FTIR
CO_2	78	64	FTIR
C-H	6	6	FTIR
C-D	1	<1	FTIR
C-T	6	3	FTIR

Achievements

- **External manifold was fabricated**
- **TIDS manifold and instruments operating procedures approved**
- **Calibration and first sample measurements completeted**

Path Forward

- **Potential upgrades to current manifold and instrumentation are being identified.**
- **TIDS will be implemented as a permanent tool for process optimization and troubleshooting.**
- **TIDS will be established as the platform for aiding the transition of analytical instrumentation from the lab to the process.**

Team Members/Contributors

- **SME's**
  - José A. Cortés Concepción
  - Rob Lascola
  - John Young
  - Bill Spencer
- **MTF**
  - Steve Murphy
  - George Thomas
- **Tritium**
  - Jon Wright
  - Don Appel
  - Joey Huckabee
  - Stephen Douglas
  - Louis Boone
  - Trey Williamson

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