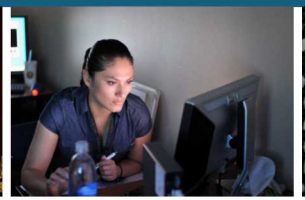
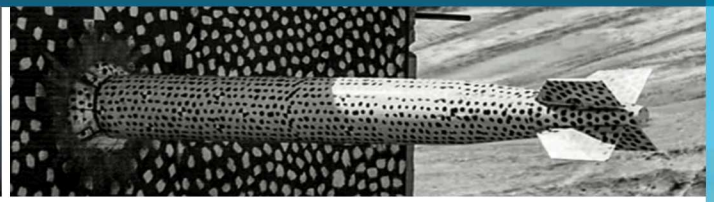
SAND2019-5148PE

Initial Findings from Gas Analysis Round Robin





PRESENTED BY

Lynelle K. Takahashi, R. M. Garcia & R. L. Jarek (with data from participants at various labs)

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Outline

Samples and Participants

Results of H_2-D_2 Vendor Gas

- SNL MS1 vs. MS2 results
- Initial Results – PNNL, AWE, U. Rochester
- H-D Quantification

Mass Cal Gas

Cal Mix H Gas

Next Steps?

Discussion

Samples and Participants

Phase 0 (non-tritiated, readily available gases)

H_2-D_2 Mixture
- Intended to test quantification of H-isotopes
- H_2 and D_2, any HD from conversion in bottle
- Faraday Detector Level H2-D2 mixture for quantification

"Mass Cal Gas"
- Faraday Detector Level
- H_2, HD, D_2, CH_4, N_2, Ar, CO_2

"Cal Mix H"
- SEM Detector Level Gases
- H_2, He, D_2, CH_4, N_2, Ar, CO_2, HCF_3, Kr, Xe, Ne

*Acknowledge Chandra Marsden & Jessica A. Bierner for initiating the round robin effort in early stages!

Participants

- SNL-NM
  - MS1 (Finnigan MAT271)
  - MS2 (Finnigan MAT271, updated SRNL electronics)
- AWE
  - Nu Evolution
- PNNL
  - Finnigan MAT271
- LANL
  - Finnigan MAT271
- University of Rochester
  - GC system
- LLNL (bottles sent 4/23/19)
  - Finnigan MAT271

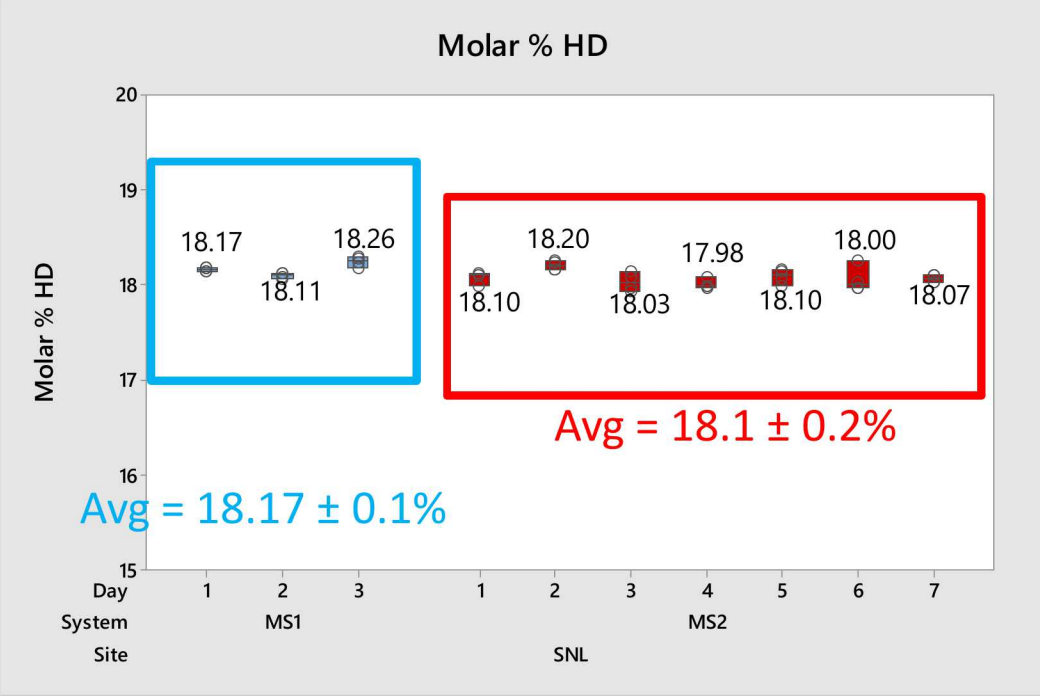
Vendor H_2-D_2 Mixture at SNL-NM

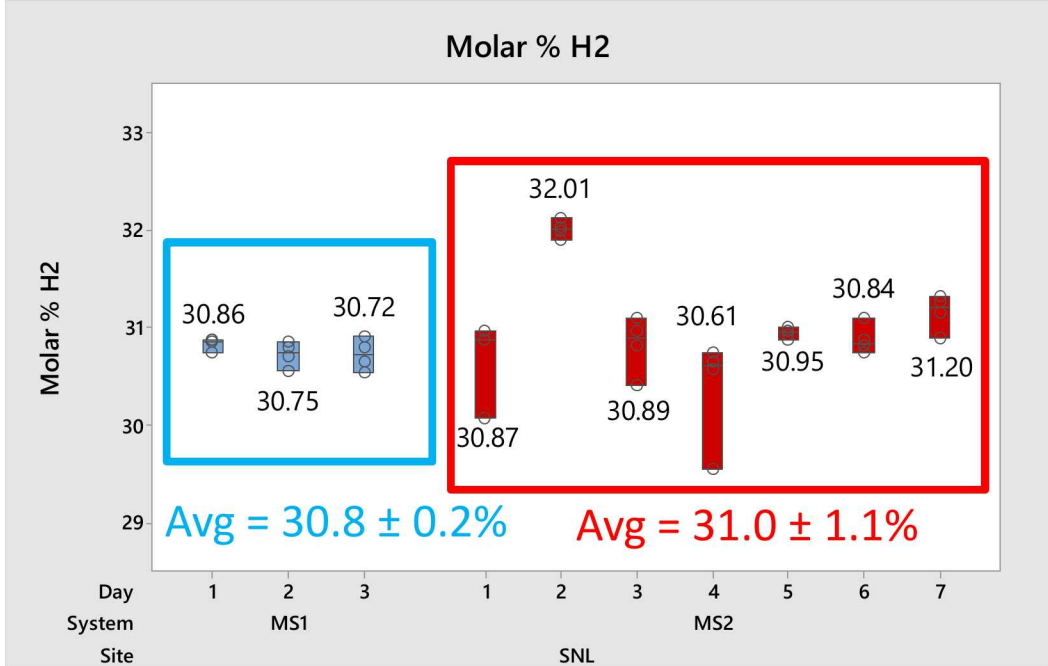
- SNL's MS1 and MS2 systems are MAT271s.
- Data collected for several days, and sensitivity calibrations performed each day
- Faraday detector used

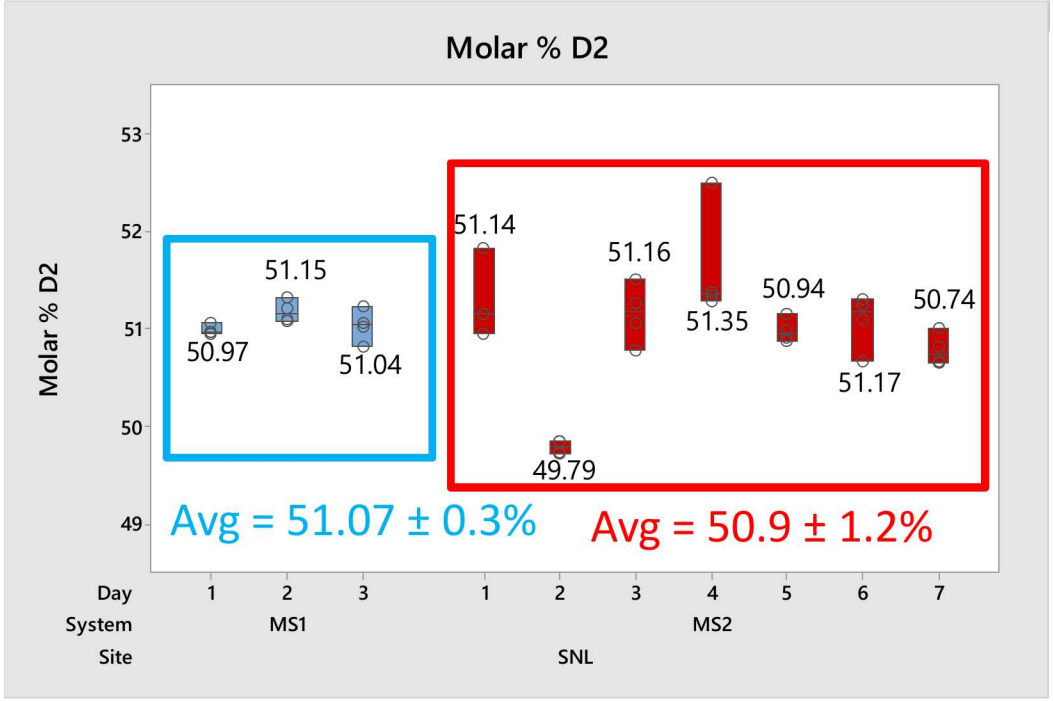
- MS2
  - Not tritium-contaminated.
  - Did not have an HD standard. HD sensitivity estimated by averaging H_2 and D_2.
  - Has updated SRNL electronics.
  - Magnet / Software still needs further optimization to reduce data scatter
- MS1:
  - Tritium-contaminated
  - HD sensitivity determined from HD in standard tritium-containing SRNL standard mixture
  - Original Finnigan electronics

Vendor H_2-D_2 Mixture At SNL-NM

- Despite larger scatter, MS2 average measured composition agrees reasonably well with MS1.
- Work ongoing to decrease MS2 measurement spread.







H_2-D_2 Mixture

	Measured Results for Vendor Mix							
	SNL-MS1	SNL-MS2	PNNL	PNNL Aliquot (SNL-MS1)	AWE	AWE Aliquot (SNL-MS2)	U. Rochester	Equilibrium (40-60) @ RT*
H_2 (%)	30.8	31.0	39.8	38.5	19.8	19.5	43.0	17.2
HD (%)	18.2	18.1	0.8	2.9	45.9	40.7	3.0	45.7
D_2 (%)	51.0	50.9	59.5	58.6	34.3	39.8	54.0	37.2
# Days Fill to Measurement	24-55	9-35	66	222	225-256	166	~60	--

- Measured composition varied greatly – non-equilibrium mixture
- Variation was observed even between sites that received similar bottle types
- HD contribution did not always correlate with time to measurement

*Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933); https://doi.org/10.1063/1.1749265*

Vendor H_2-D_2 Mixture

	Back-Calculated* H/D for Vendor Gas Mixture							
	SNL-MS1	**SNL-MS2**	**PNNL**	**PNNL Aliquot (SNL-MS1)**	**AWE**	**AWE Aliquot (SNL-MS2)**	**U. Rochester**	***Vendor Certification***
H	39.9%	40.1%	40.2%	40.0%	42.7%	39.9%	44.5%	*35.0 %*
D	60.1%	60.0%	59.9%	60.1%	57.3%	60.2%	55.5%	*65.0%*
H/D	0.66	0.67	0.67	0.67	0.75	0.66	0.80	*0.54*

*Back calculated original composition by adding half of HD to H_2 and D_2.

- Generally, good agreement in H/D ratio despite gas mixture instabilities.
  - Future plans to examine bottle surface vs. gas stability
- AWE H/D ratio higher than Finnigans – lower pressure, larger volume, calibration method?
- Largest difference observed in GC method – calibration standard?
- Finnigan instruments (blue columns) showed ~1% relative spread in measured H/D ratio.

Mass Cal Gas

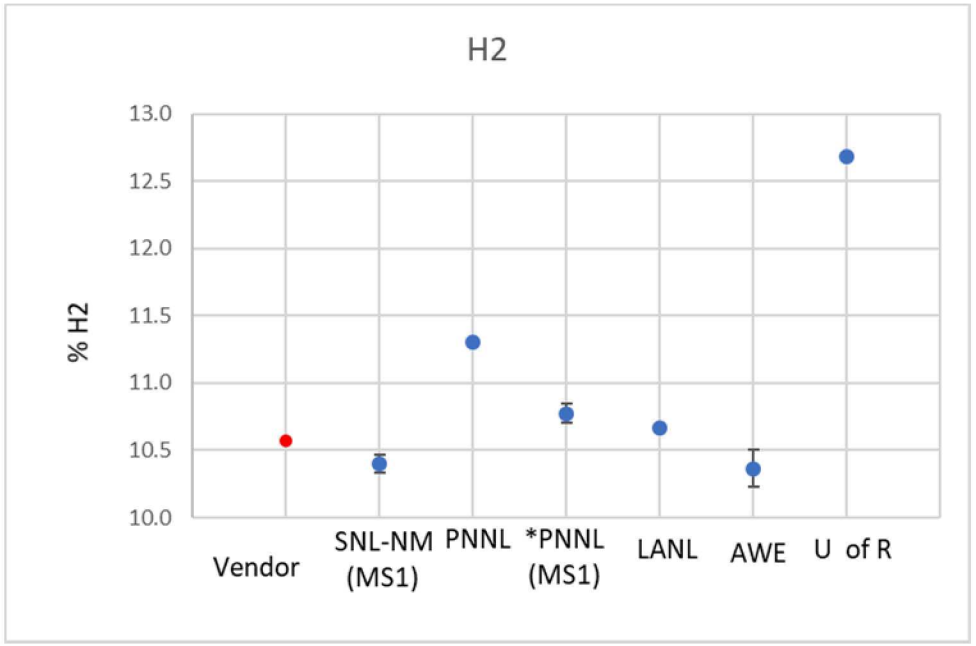
	Measured Results for Mass Cal Gas							
	Vendor Certification *(1997)*	**Vendor Cert. @ Eq.**	**SNL-MS1**	**PNNL**	**PNNL Bottle Aliquot (MS-1)**	**LANL**	**AWE** **Renormalized*	**U. Rochester** **Renormalized*
H_2	20.0	10.6	10.4 ± 0.1	11.3	10.8	10.7	10.4 ± 0.1	12.8 ± 0.0
HD	0.0	18.9	17.4 ± 0.1	18.8	17.4	17.1	17.7 (NR)	17.1 ± 0.0
D_2	20.0	10.6	11.1 ± 0.1	11.3	11.1	11.1	10.3 ± 0.1	9.9 ± 0.0
CH_4	15.0	15.0	15.2 ± 0.0	15.0	15.1	15.6	16.8 ± 0.3	NR
N_2	15.1	15.1	15.3 ± 0.1	14.6	15.2	15.4	14.2 ± 0.1	NR
Ar	14.9	14.9	15.4 ± 0.0	14.4	15.2	15.2	15.5 ± 0.1	NR
CO_2	15.0	15.0	15.2 ± 0.0	14.7	15.3	14.9	15.1 ± 0.1	NR
H/D	1.00	1.00	0.97	1.00	0.98	0.98	1.00	1.16

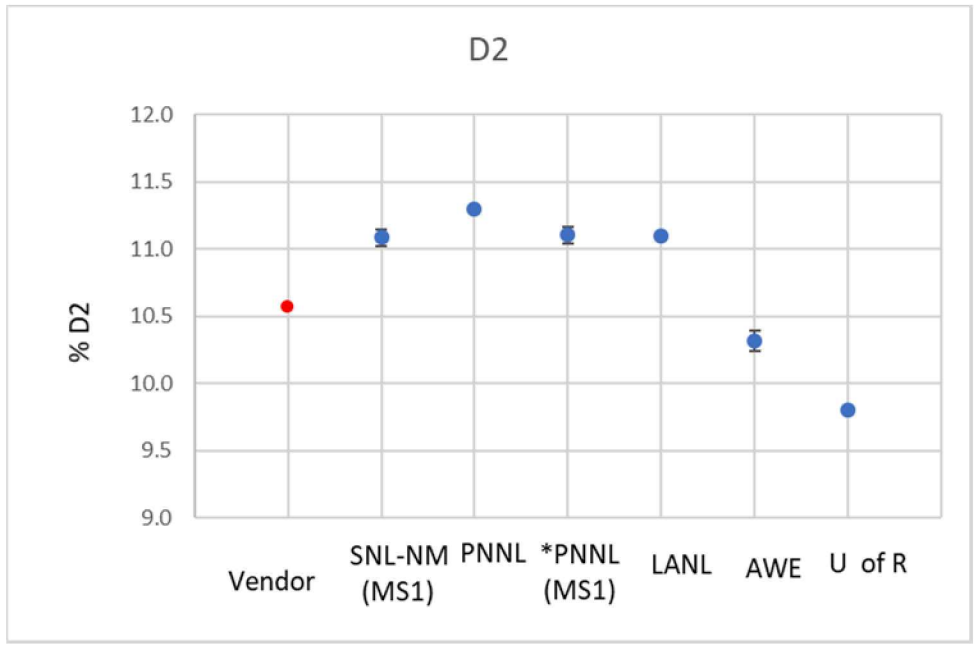
*Data was renormalized to the average of SNL-MS1, PNNL and LANL to make comparison easier.

- Finnigan systems again show good agreement in calculated H/D ratios.
- Slight difference observed in U. Rochester GC method.

NR = not reported

Mass Cal Gas





Finnigan systems show good agreement.

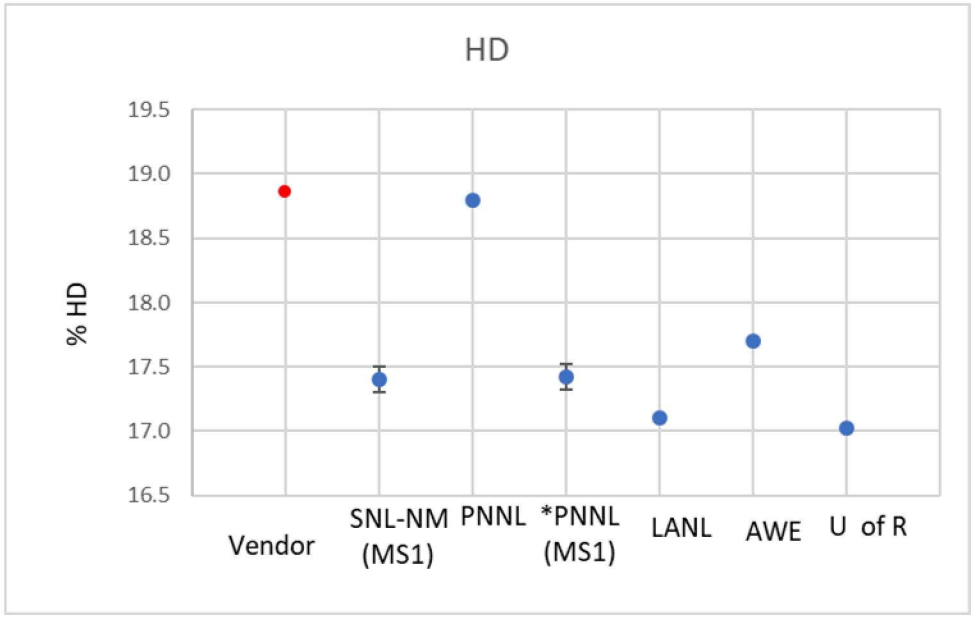
- MS1 error bars estimated only from repeated measurement (precision).

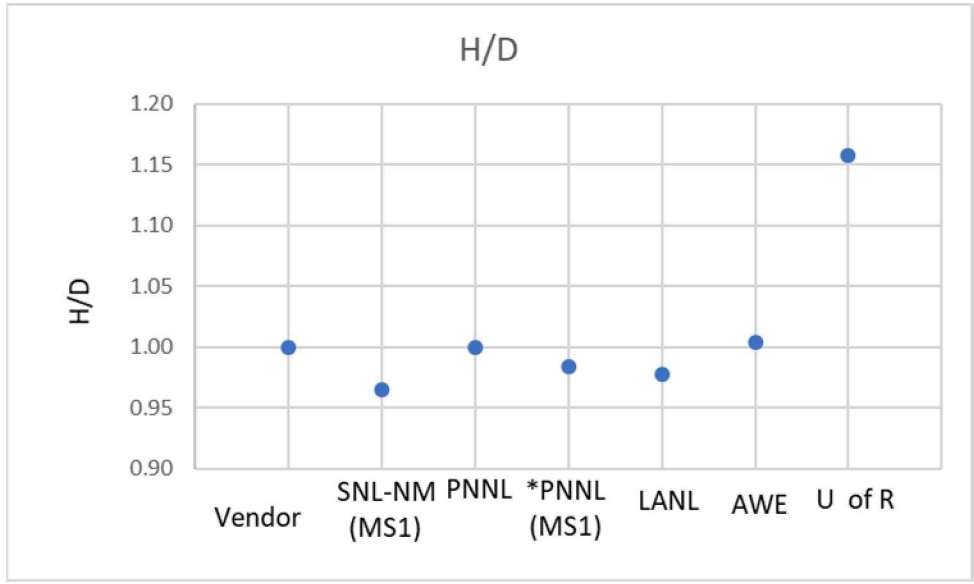
Slight difference observed in U. Rochester GC method.

Measured values differed from vendor-certified value (1997) due to HD formation.

- Expected equilibrium values shown in red.

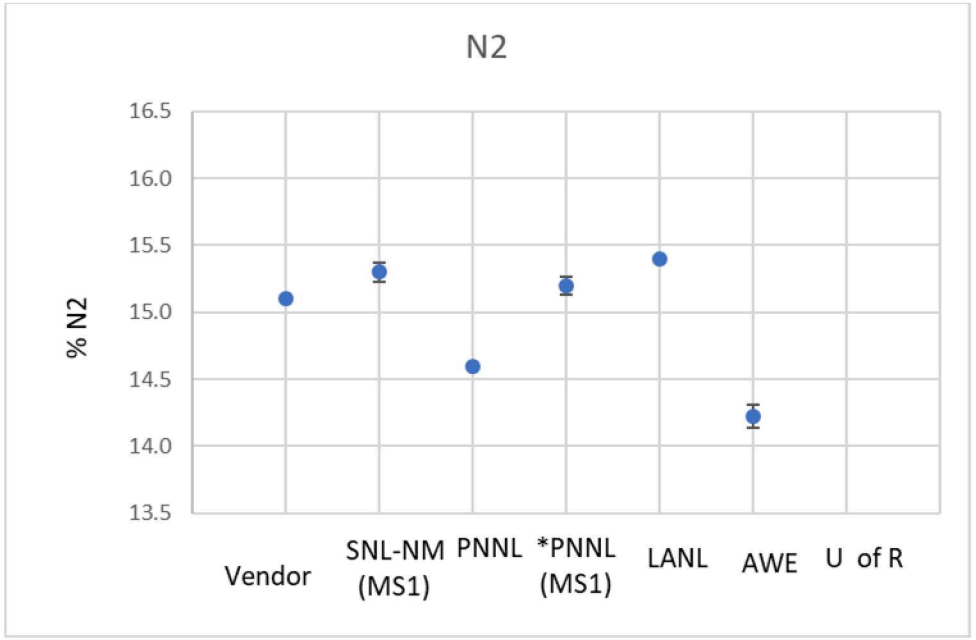
Mass Cal Gas

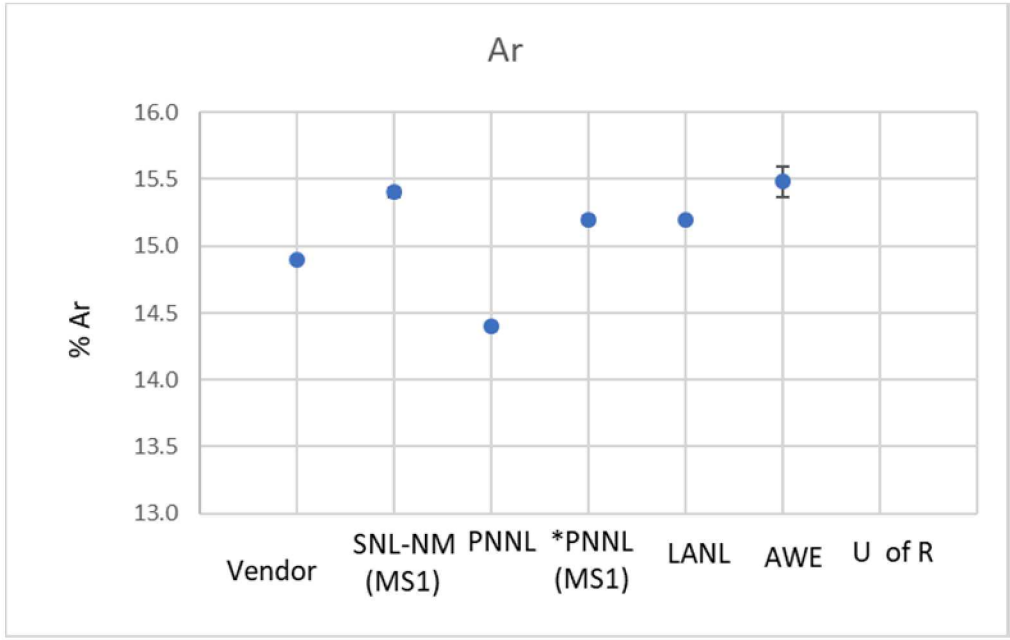




- Finnigan systems again show good agreement in calculated H/D ratios.
  - MS1 error bars estimated only from repeated measurement (precision).
- Slight difference observed in U. Rochester GC method.
- Expected equilibrium HD formation from vendor certified H_2 and D_2 starting values shown in red.

Mass Cal Gas





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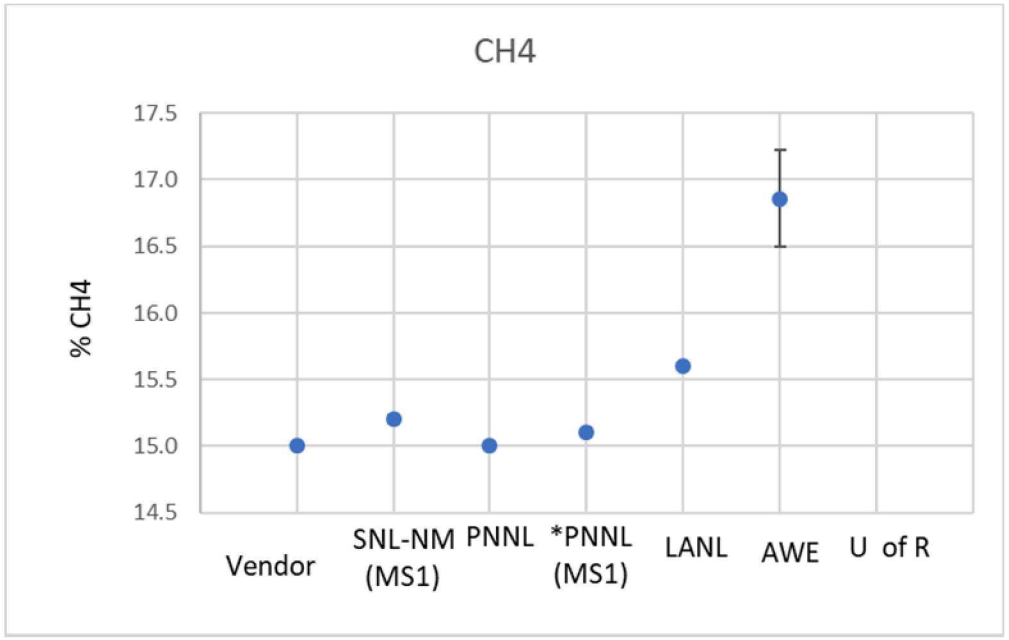
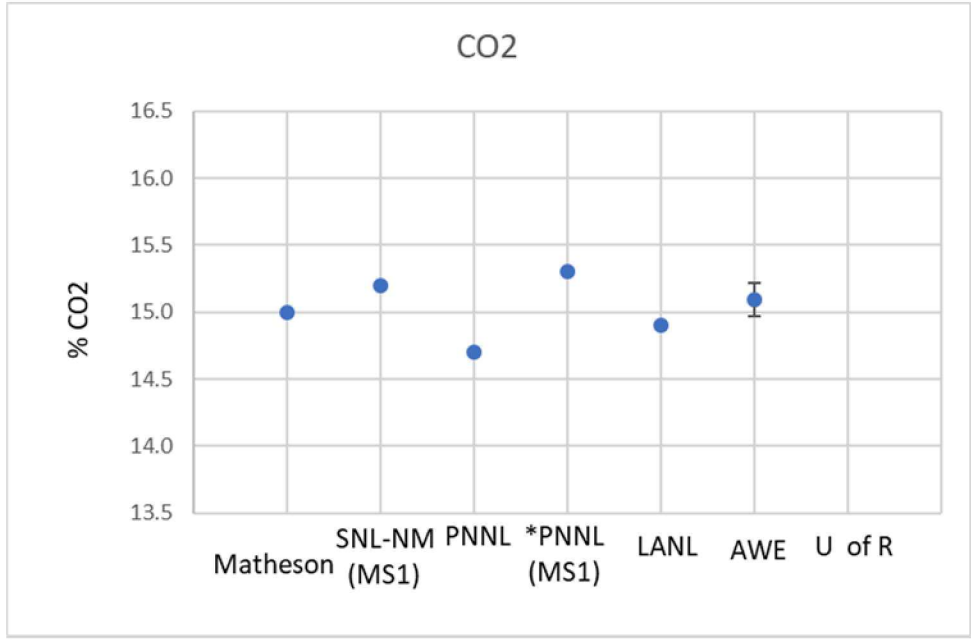
Mass Cal Gas





- Finnigan systems again show good agreement.
  - MS1 error bars estimated only from repeated measurement (precision).

Cal Mix H Gas

- CalMix H has large Ne component, and lower levels of other gases.
  - Test consistency of SEM detector measurements
- Higher relative variation across the sites for certain species (orange rows)

** Uncertainty in the HCF_3 sensitivity calibration*

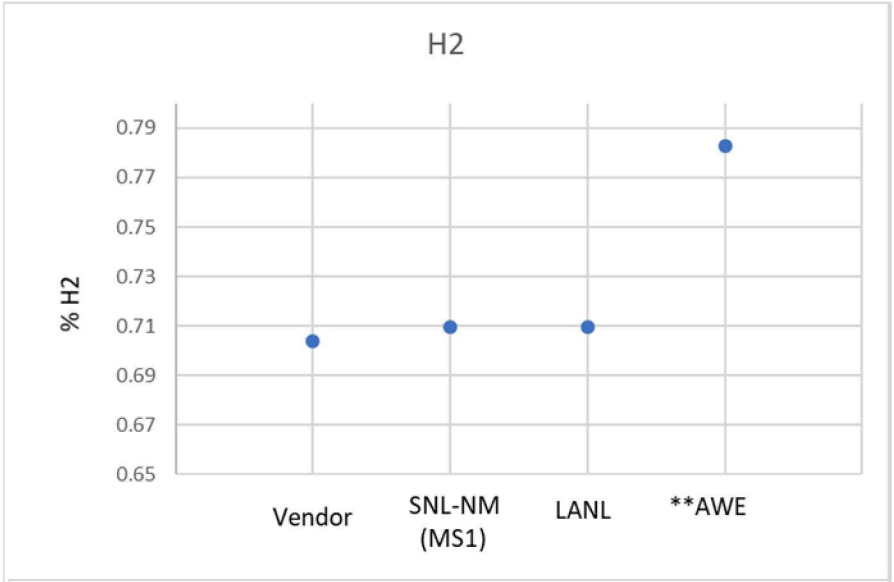
*** Renormalized for absence of N_2*

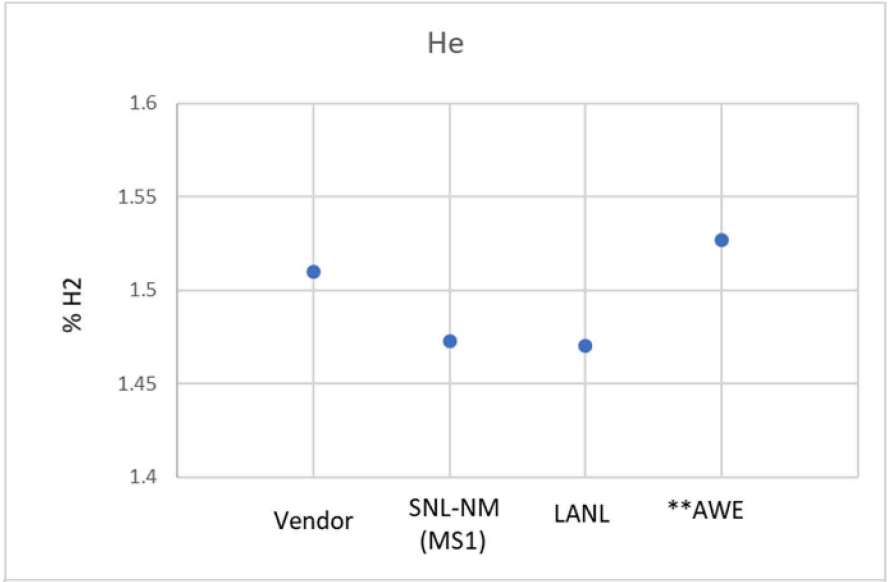
NR = not reported

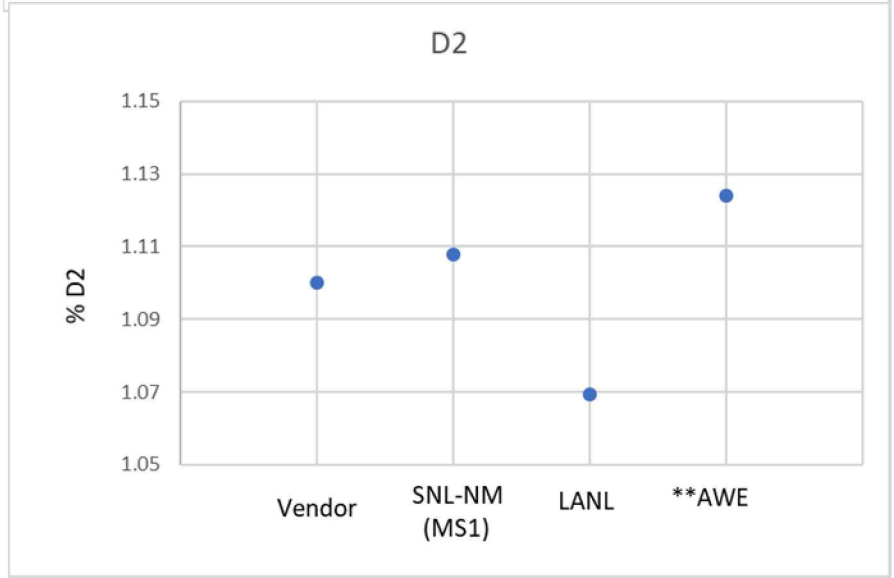
	Measured Results for Cal Mix H Gas Composition				
	Vendor Certification	**SNL-MS1**	**LANL**	AWE	**AWE** **Renormalized
H_2	0.704	0.710	0.710	0.785	0.783
HD		0.000	0.017	0	0.000
He	1.51	1.473	1.471	1.531	1.527
D_2	1.1	1.108	1.069	1.127	1.124
CH_4	0.382	0.390	0.383	0.482	0.481
Ne	92.23	92.283	*93.017	91.708	91.473
N_2	0.251	0.259	0.253	NR	0.256
Ar	0.252	0.267	0.258	0.32	0.319
CO_2	0.221	0.222	0.216	0.245	0.244
HCF_3	1.2	1.326	*0.553	1.179	1.176
Kr	0.75	0.724	0.705	0.882	0.880
Xe	1.4	1.238	1.349	1.741	1.737
H/D	0.64	0.64	0.67	0.70	0.70

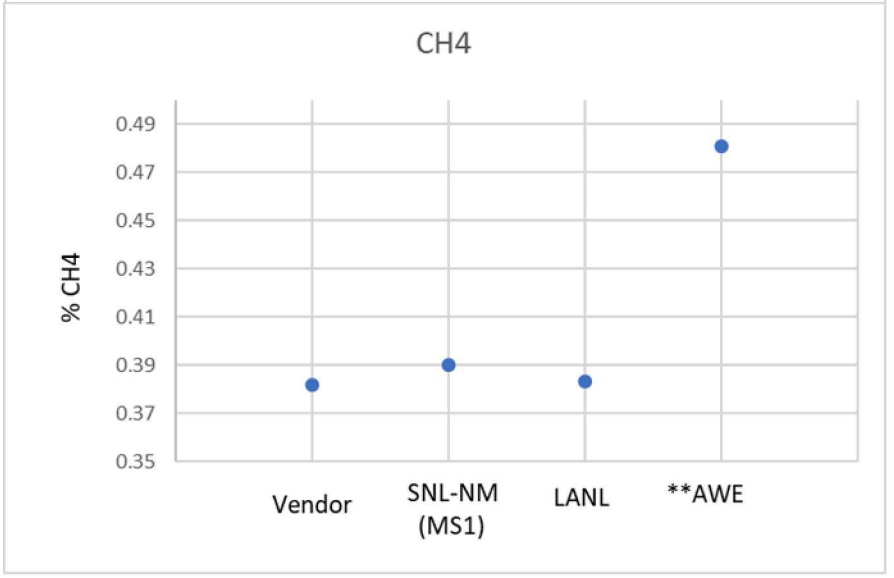
Cal Mix H Gas

Limited data for SEM-level gases. LLNL results pending.









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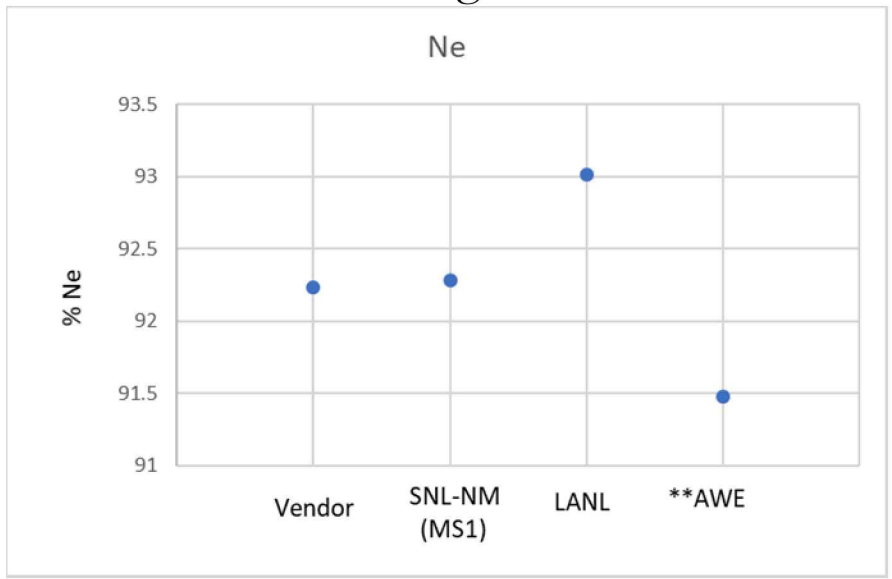

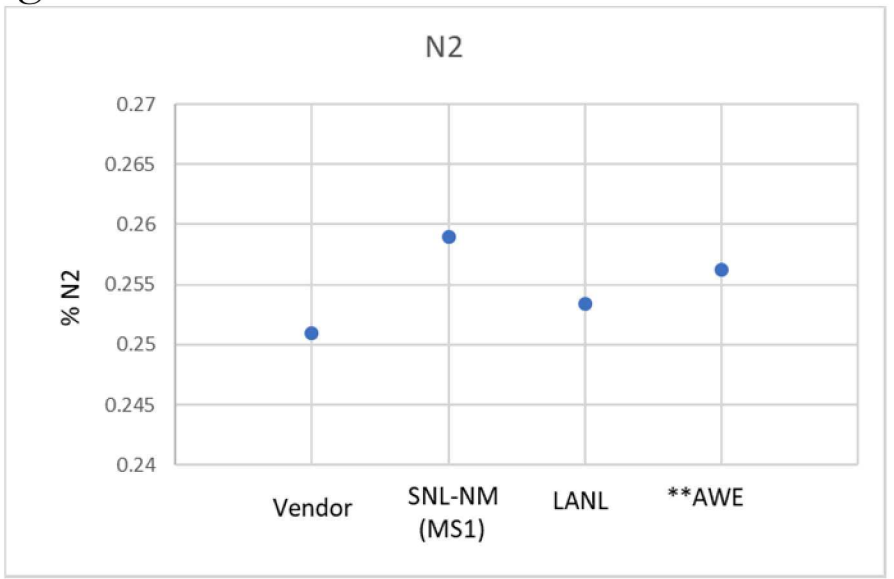

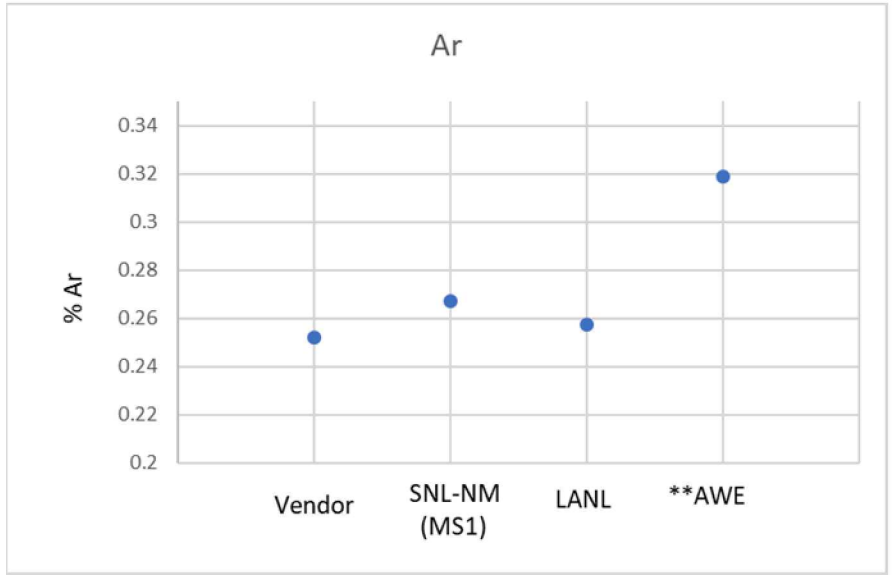

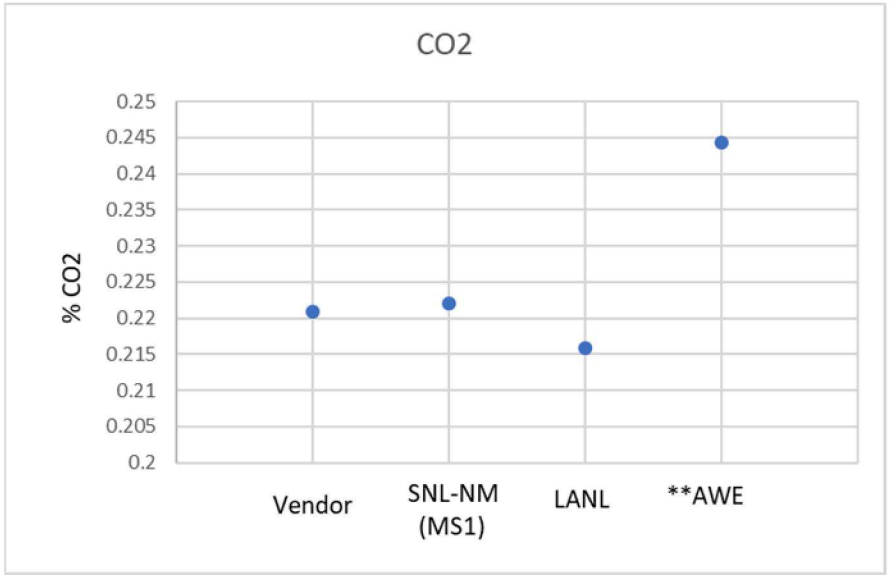

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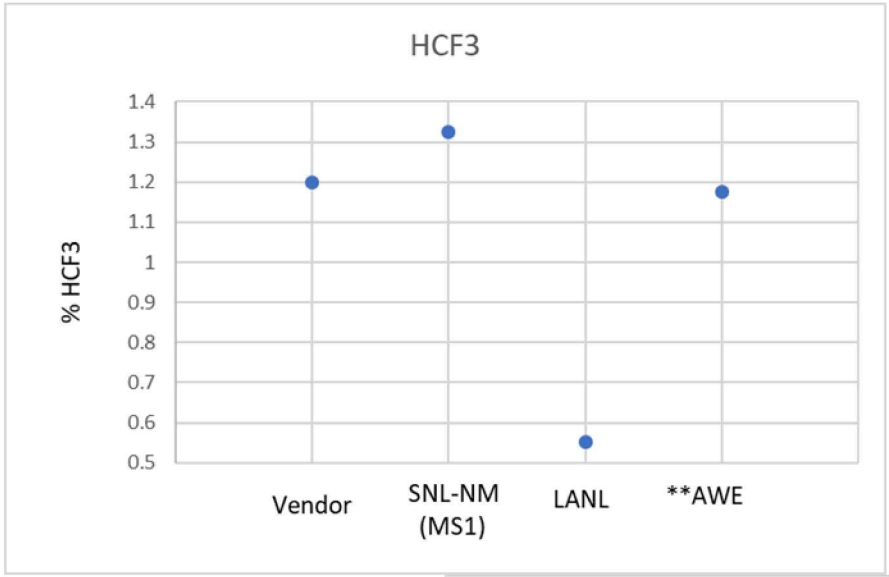
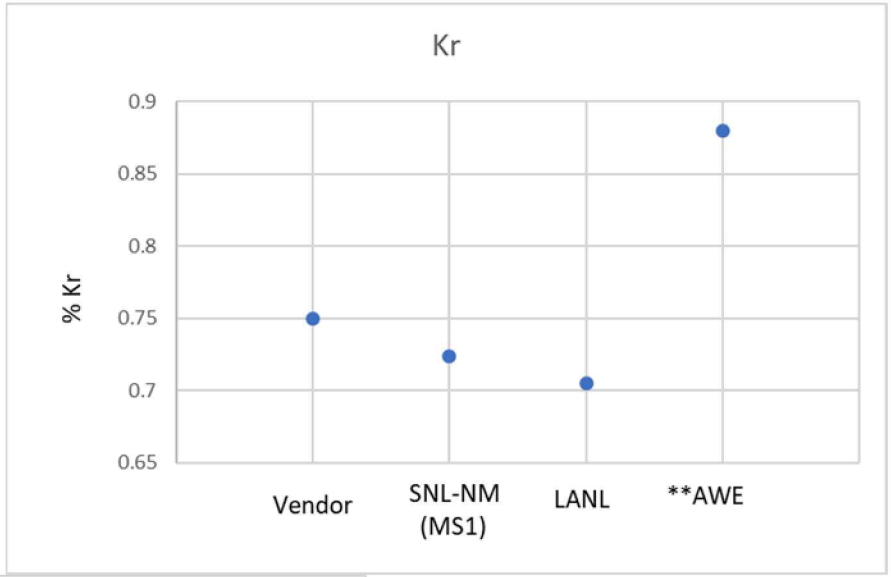
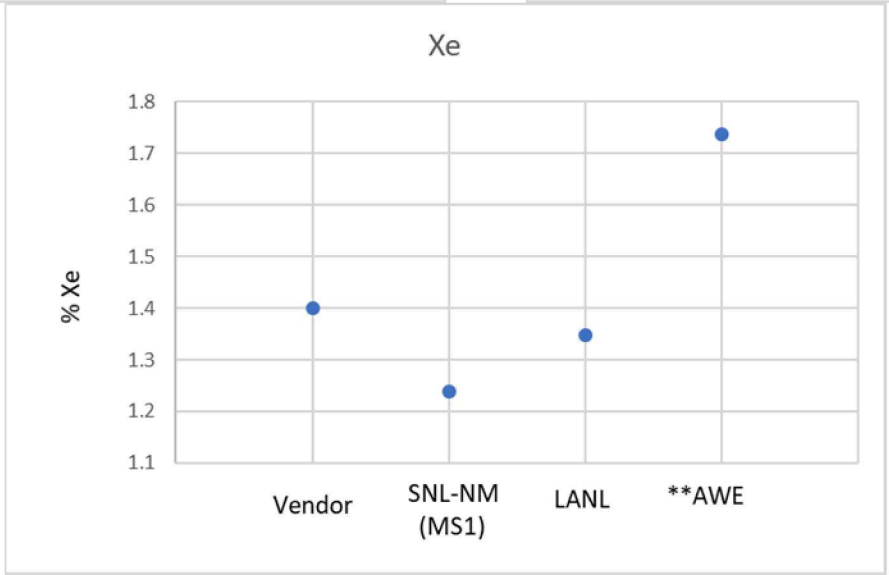
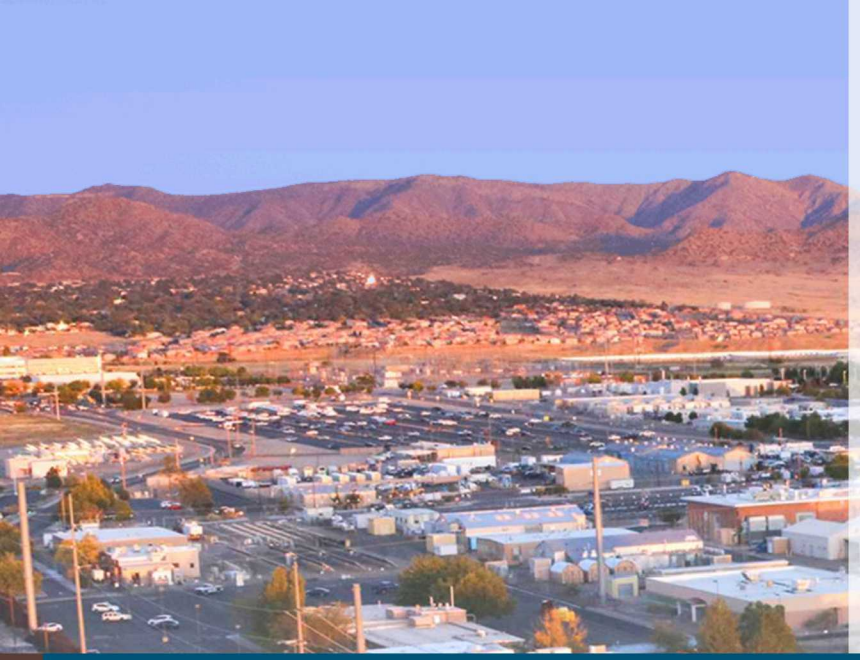






Summary

- Finnigan mass spectrometers showed good agreement for H_2-D_2 mixture and Mass Cal Gas.
- AWE Nu system showed some differences compared to the Finnigans – differences in the instrument or calibration method?
- U. Rochester GC method showed the largest differences. Method is still under development.
- Non-equilibrium gas mixtures appeared to change with time, with rates depending on particular bottles.
  - Future iterations may need to use equilibrated mixtures and/or passivated bottles.
- Cal Mix H Gas shows higher variation across sites for certain species
  - H/D ratio from AWE looks more consistent with other sites – lower H_2 & D_2 partial pressure, less HD?
- Additional data still incoming
  - LLNL bottles shipped late April 2019.
  - LANL H_2-D_2 mixture results still pending.
  - Other sites want to participate?
- Next steps… tritiated gases?



Round Robin Discussion

Discussion

Variables

Bottle history, aliquoting practices

Gas introduction method / configuration

Ionization

Transmission

Detection

Calibration Frequency & Method

Standards Used for Calibration

Scan Experiments – consistency in calibrant & sample measurement

Peak Definition – point density

Next Phase

Use of passivated bottles and/or equilibrated gas mixtures

Pre-measure bottles prior to sending

Multiple measurements desirable, promptly after receiving

Tritium-containing mixtures from Savannah River?

Bottles For Vendor H_2-D_2 Mixture

AWE

Bottles - AVC-304L-05SF4-500

- Cold formed female NPT threads
- 304L Stainless Steel
- Standard cleaning (SC-10)

Valve - AVC-SS-4BK-V51-VA

- Stainless Steel Bellows Sealed Valve
- PCTFE stem tip
- SC-11 cleaned
- 316 Stainless Steel
- Butt welded female VCR fitting

PNNL / SNL / LANL / U. Rochester

Bottles – SS-4CS-TW-50

- 316 Stainless Steel
- SC-11 cleaned

Valve - SS-4BK-TW-VA

- Stainless Steel Bellows Sealed Valve
- PCTFE stem tip
- SC-11 cleaned
- 316 Stainless Steel