Detection and monitoring tools for quantification of hydrogen releases, benchmark against methane

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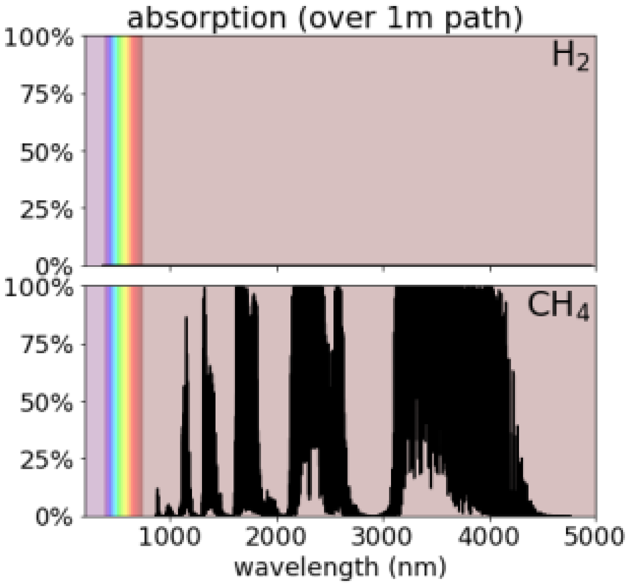
Workshop on Environmental Impacts of Hydrogen
April 1, 2022

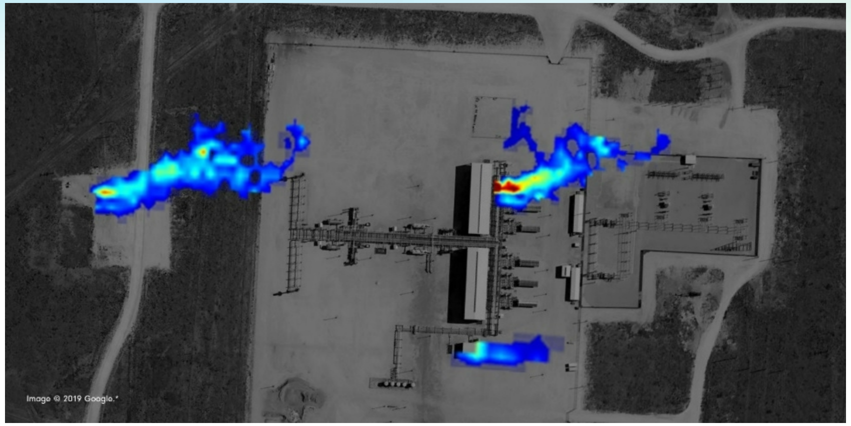
Part 1

OPTICAL DETECTION STRATEGIES FOR HYDROGEN LEAKS: WHAT WORKS AND WHAT DOESN’T

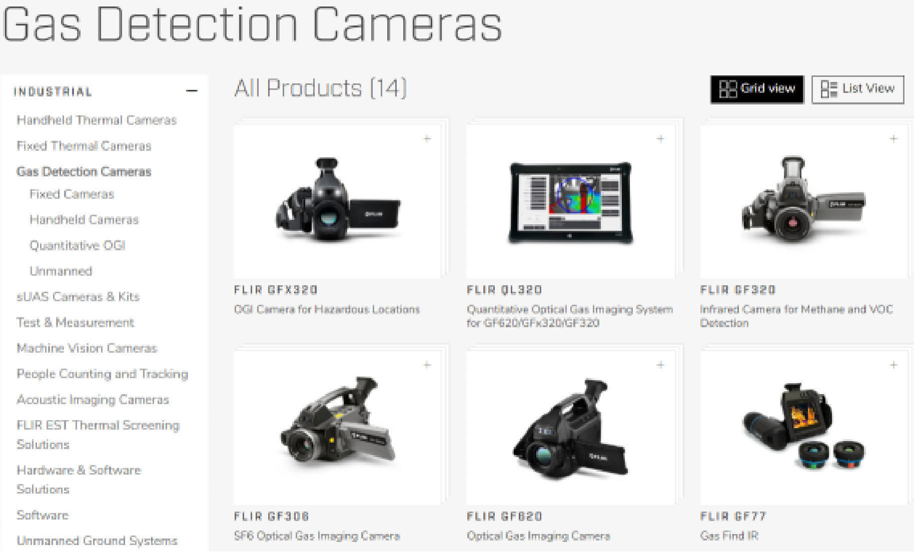
Commercial products exist for imaging methane (and other hydrocarbon) leaks

- Products for a range of length scales
  - Aerial imaging to detect large leaks
  - Handheld imaging to detect small leaks
- Quantitative concentration and leak rate information
- Use infrared absorption features of methane
- Absorption features not present for hydrogen





Gas mapping LiDAR from https://www.bridgerphotonics.com/blog/gas-mapping-lidartm-explained



Gas Detection Cameras

All Products (14)

FLIR GFX320
OGI Camera for Hazardous Locations

FLIR QL320
Quantitative Optical Gas Imaging System for GF620/GFx320/GF320

FLIR GF320
Infrared Camera for Methane and VOC Detection

FLIR GF306
SF6 Optical Gas Imaging Camera

FLIR GF620
Optical Gas Imaging Camera

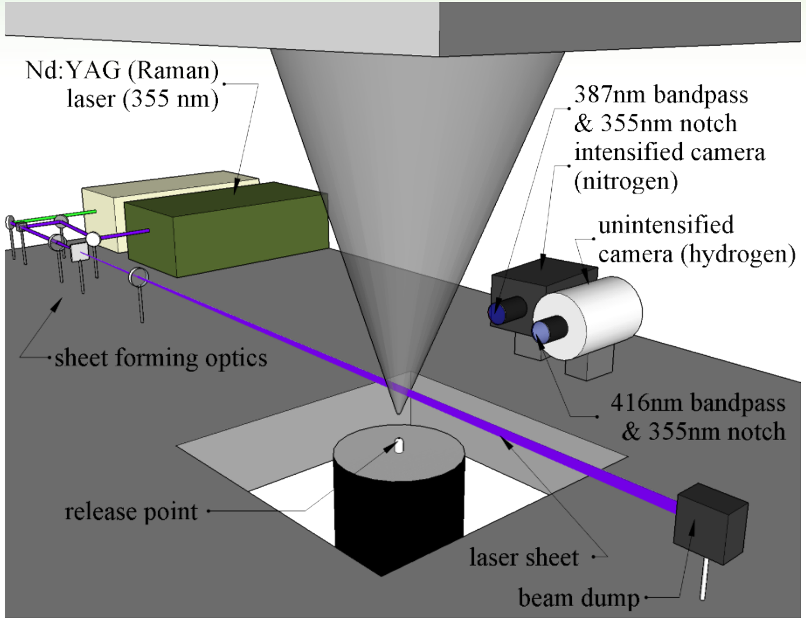
FLIR GF77
Gas Find IR

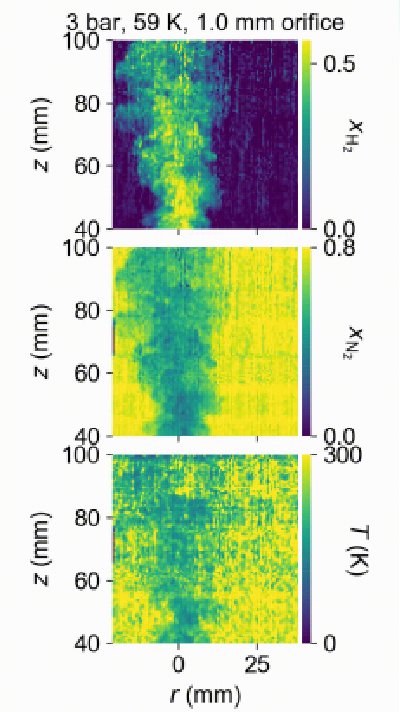
Gas detection cameras from FLIR (FLIR.com)

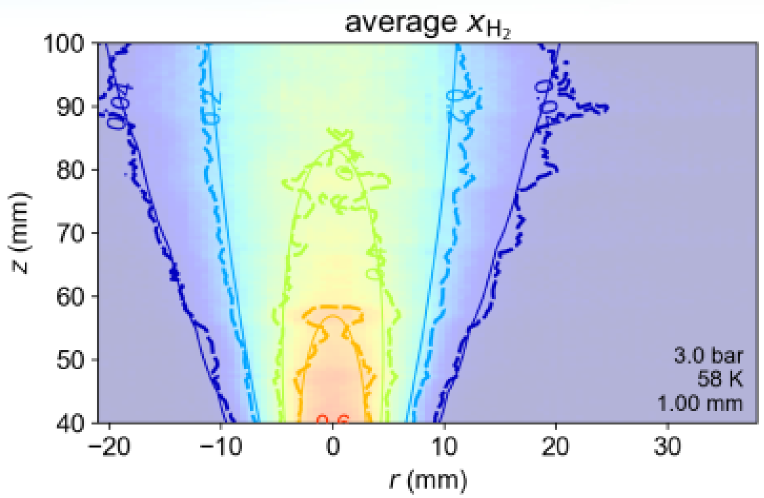
Common optical techniques to visualize gas flows

Technique	Principle	Works with H_2	Gas specific	Quantitative
Shadowgraphy	Refractive index gradients bend light rays as they pass through density variations	✓		
Schlieren	Same as shadowgraphy except knife edge enables focused image to form	✓		✓
Fluorescence	Photons are absorbed by molecules at a resonant transition and light is reemitted at a shifted wavelength		✓	✓
Absorption	Gases have absorption features for certain wavelengths of light		✓	✓
Rayleigh scattering	Elastic scattering off of different molecules is proportional to their cross-section and number density	✓		✓
Raman scattering	Inelastic scattering off of different molecules gives each component a spectral fingerprint	✓	✓	✓

We have used Raman imaging of room temperature and cryogenic hydrogen releases to validate a dispersion model



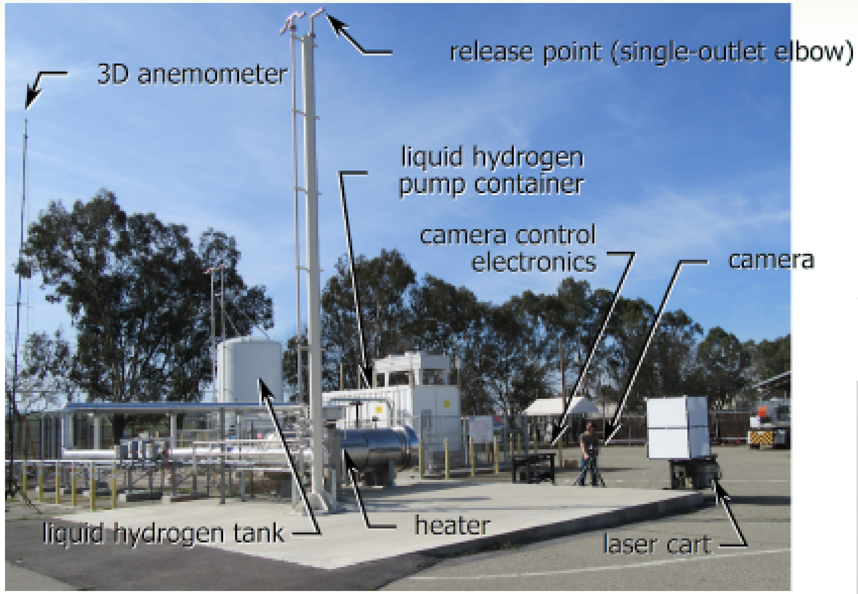


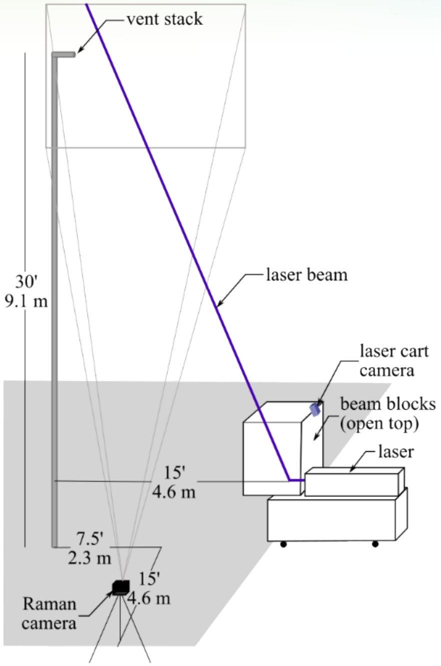


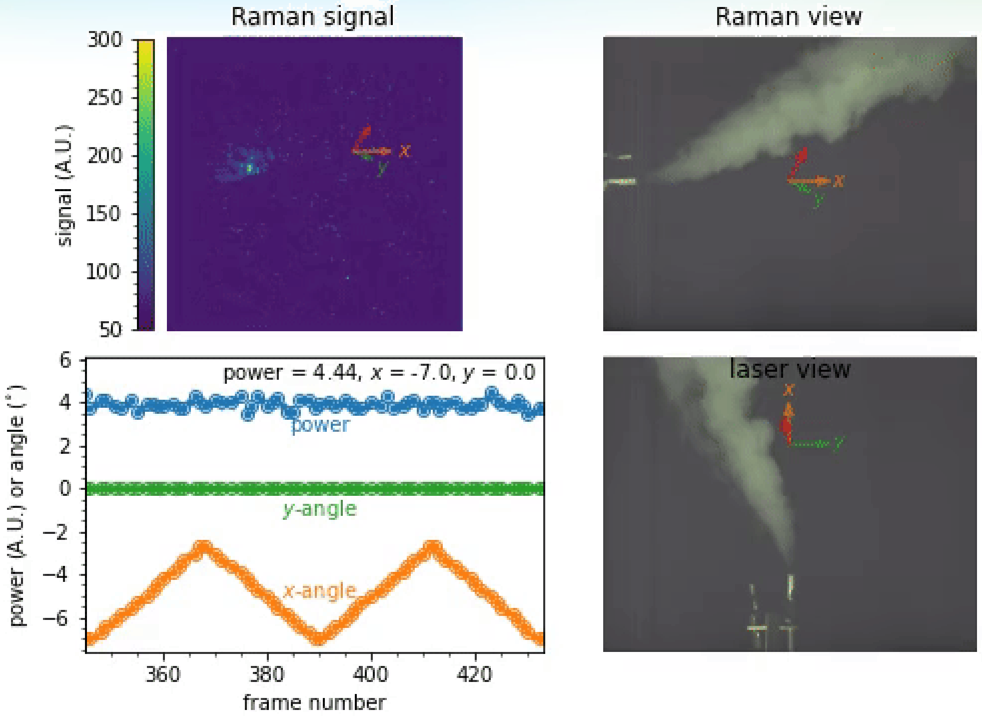
- Requires high-powered illumination (laser) due to low signals
  - Can only image small portion of the plume (laser sheet width) at a time
  - Multiple image planes stitched together
- Unique wavelength signal enables suppression of signal from scattering off of water vapor (Mie scattering)

- Results in 2D image of dispersion characteristics
- Average concentration (and temperature) used to validate model

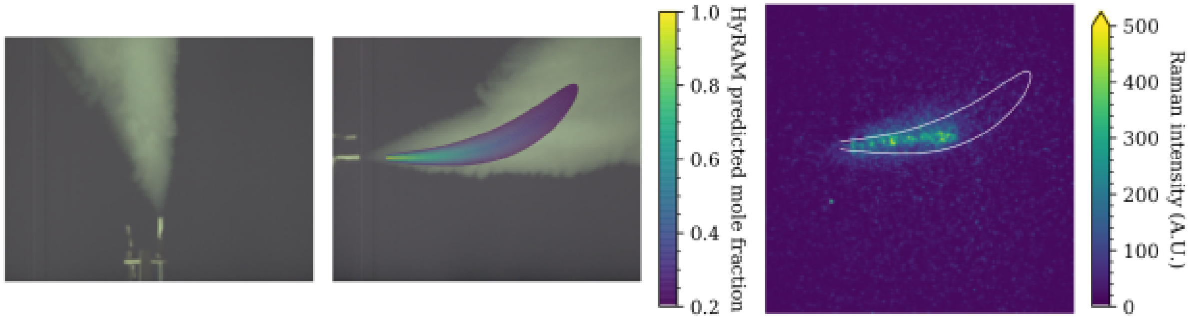
Large-scale Raman scattering experiments have demonstrated technique for vent stack dispersion



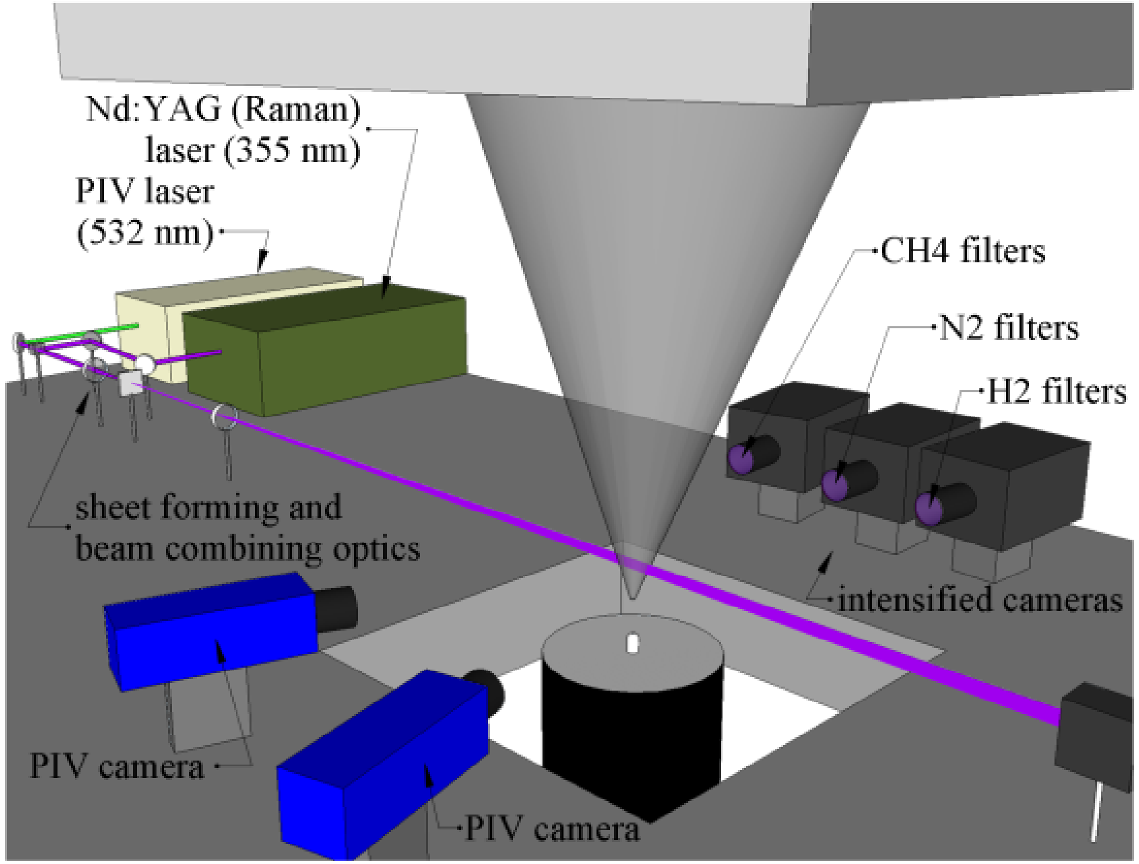




- Similar to lab-scale experiments, requires high-powered laser illumination
  - Raster laser through plume (signals from flood illumination too small)
  - Challenging to quantify concentration with small signals
- Signals can be large enough to detect from > 10m away



Currently using Raman imaging to measure dispersion behavior of hydrogen/methane blends in the lab

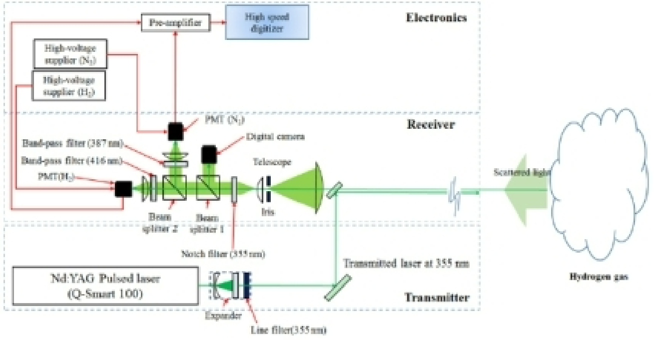


- Signals specific to molecules in the blends
  - Can differentiate between hydrogen and methane
  - Quantify concentration of all species
- 2D image of dispersion characteristics
- Will tell us whether hydrogen and methane stay well-mixed as they disperse
- Separate experiments to quantify ignition and flame characteristics of blends

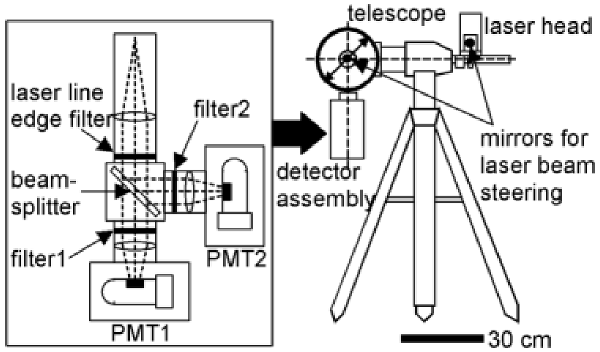
Summary of optical techniques for hydrogen detection

- Shadowgraphy and Schlieren possible
  - Require ordered background and image processing
  - Difficult to quantify
  - Not gas specific
- Fluorescence would require seeding with another molecule
- Absorption not possible because hydrogen lacks strong absorption features
- Rayleigh scattering possible
  - Requires high power illumination
  - Not gas specific
  - Affected by Mie scattering (e.g. condensed water vapor in cryogenic plumes)

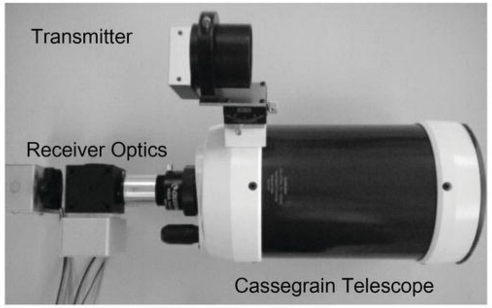
- Raman scattering has been demonstrated
  - Small signals mean high powered illumination and sensitive detectors needed
  - Several groups working on miniaturizing Raman based detection systems



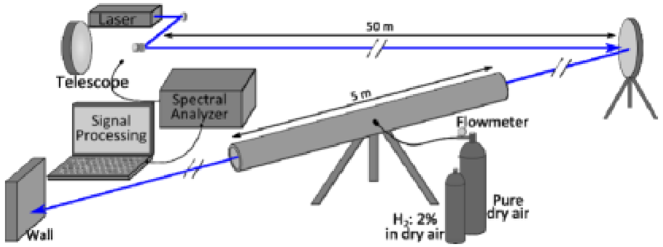
Choi *et al* (2019) *DOI: 10.1088/1361-6501/ab0260*



Ninomiya et al (2007) DOI: 10.1117/1.2784757



Shiina, 2018 DOI: 10.5772/intechopen.74630



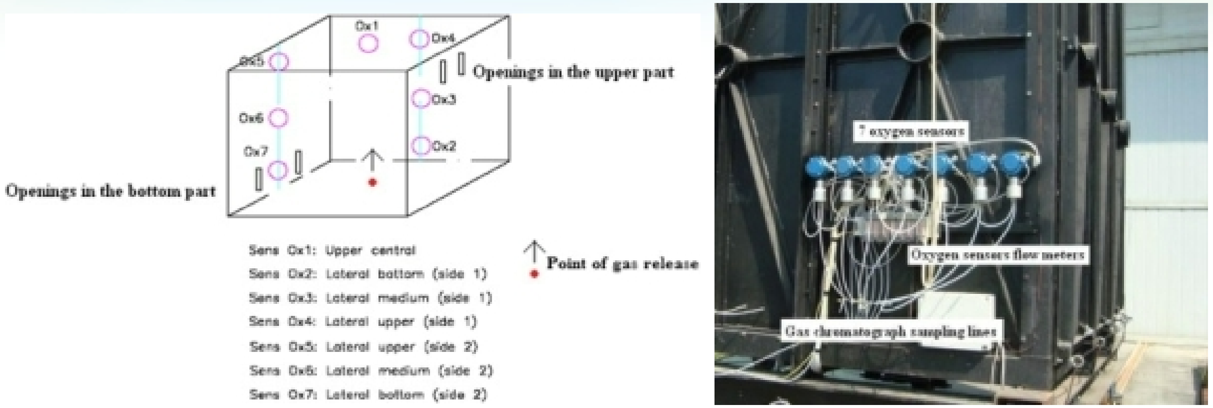
Liméry et al (2017) DOI: 10.1364/OE.25.030636

Part 2

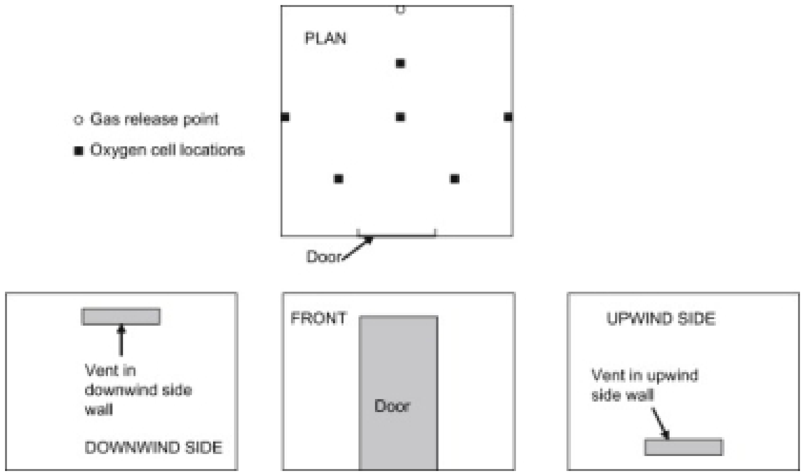
LITERATURE REVIEW ON NATURAL GAS AND HYDROGEN BLENDS: KEY RESULTS

Many experiments rely on point sensors for measuring dispersion

- Performed literature review of experiments on the release behavior of hydrogen and natural gas blends
- Several different detection methods were identified:
  - Oxygen sensors to detect the displacement of oxygen in an enclosed test cell
  - Handheld combustible gas sensors were used to inspect test sections for leaks prior to testing



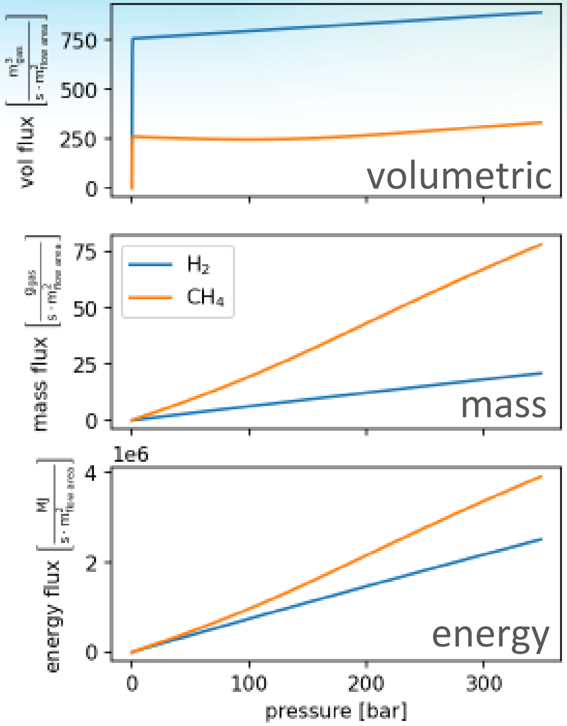
Marangon, Carcassi (2014) DOI: 10.1016/j.ijhydene.2013.10.159

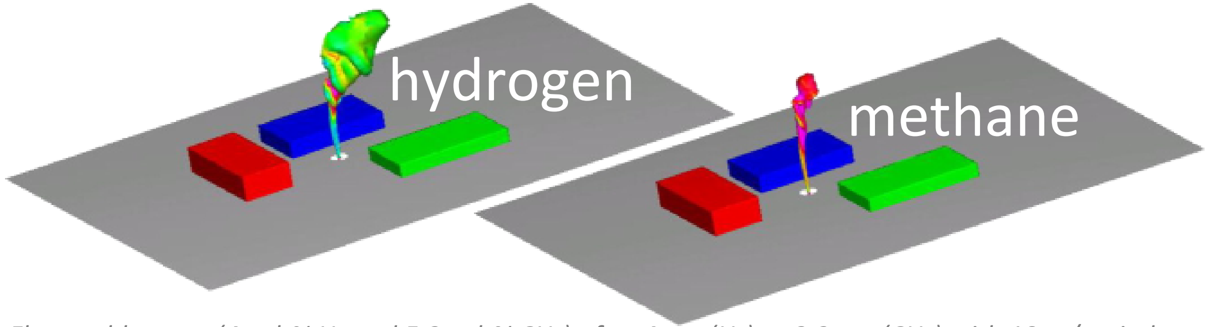


Lowesmith et al (2009) 10.1016/j.ijhydene.2009.01.060

As hydrogen content increases in blends with methane (or hydrogen replaces methane), the behavior changes

- Relationships between pressure, flow rate, rate of pressure drop, and the Reynolds number have been evaluated to analyze fixed simulated leaks
  - Volumetric flowrate of hydrogen higher than for methane at fixed pressure
  - Mass and energy flow rate of methane higher than hydrogen at fixed pressure
- As percentage hydrogen in CH_4-H_2 blends increases, dispersion behavior changes
  - Diffusion increases
  - Buoyancy increases (concentration at top of an enclosure increases faster than for methane)



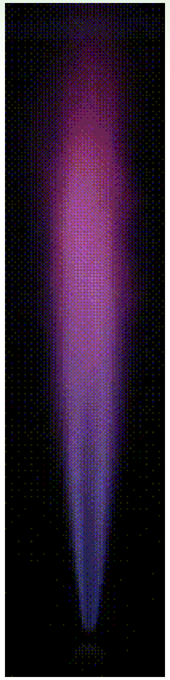


Flammable mass (4 vol-% H_2 and 5.3 vol-% CH_4) after 4 sec (H_2) or 3.2 sec (CH_4) with 10 m/s wind from a 20 cm diameter leak from an 11 bar pipeline

Wilkening, Baraldi (2007) DOI: 10.1016/j.ijhydene.2007.04.022

Summary

- Hydrogen is challenging to detect optically
  - Raman scattering can be quantitative, but requires lots of light and sensitive detectors
  - Most experiments use more conventional point sensors
  - Other area leak monitoring technologies may exist (e.g. ultrasonic) but were not discussed here
- Hydrogen disperses differently from methane
  - Hydrogen is more diffusive and buoyant than methane
  - For a given pressure and leak size, the energy and mass released will be less for hydrogen than methane
  - For a given pressure and leak size, the flammable plume of hydrogen will likely be larger than the flammable plume of methane



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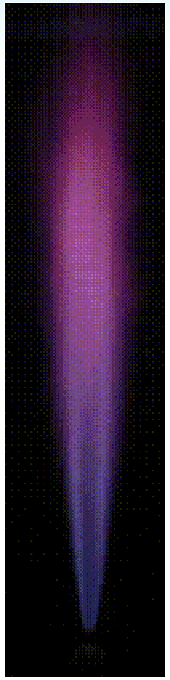


Thanks for funding support from:

- United States Department of Energy, Energy Efficiency & Renewable Energy, Hydrogen and Fuel Cell Technologies Office, Safety, Codes, and Standards subprogram managed by Laura Hill
- Industry support including the OEM Group at the California Fuel Cell Partnership, Linde, and Shell
- Air Liquide and partners

Schlieren imaging

- Measures gradients in density (1st derivative)
- For quantitative measurements:
  - Calibrated schlieren – uniform light source, light intensity quantifies refraction angles
  - Rainbow schlieren – color cutoff filter in place of knife edge, color quantifies refraction angles
  - Diverging light background oriented schlieren (BOS) – pixel offset from original position determines refraction angle
- BOS (using sunlight) possible for H_2, however:
  - Need semi-ordered background
  - Density gradients caused by both temperature and composition
  - Line-integrated, total refraction measured, extremely complex to quantify, even with tomography
  - No symmetries for an open plume

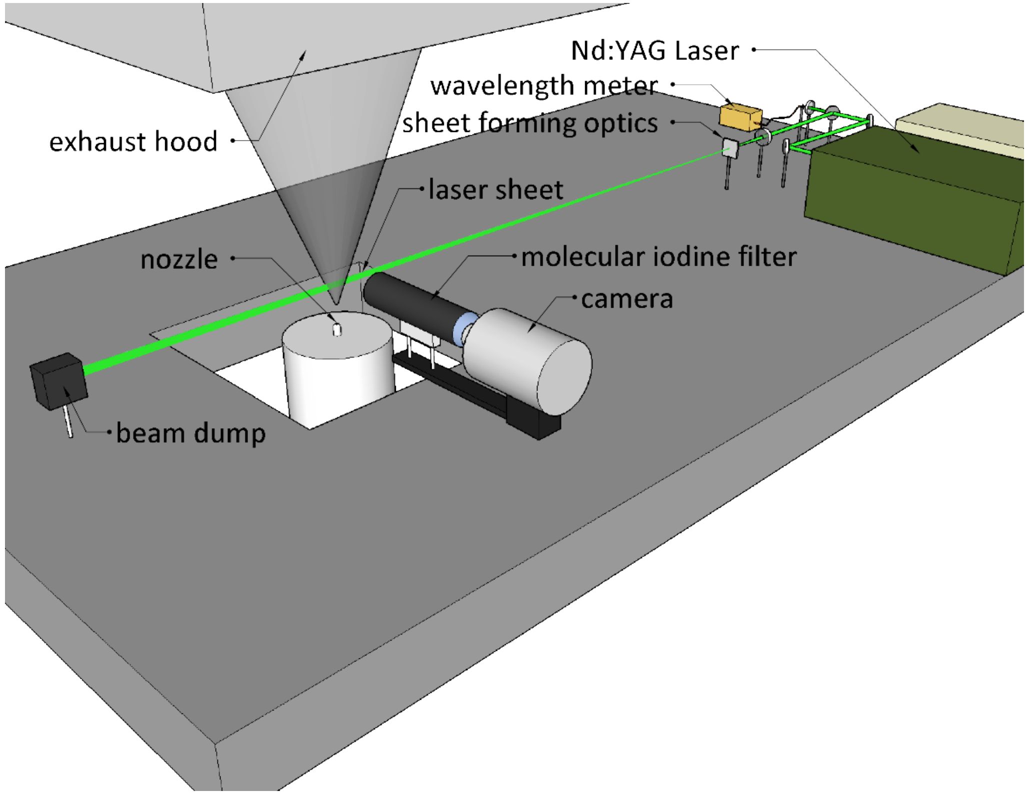
Fluorescence

- OH fluorescence possible, but only for flames, not unignited H_2
- Unignited concentration measurement would require seeding hydrogen with fluorescent tracer material (aliphatic ketones like acetone or 3-pentanone often used)
  - For cryogenic H_2, no gaseous or liquid options at LH_2 temperatures
  - Very challenging to get solid particles dispersed in liquid, and get them to follow gas flow during phase change

Rayleigh scattering

H_2 Rayleigh cross-section ≈ 10^{-27} cm^2

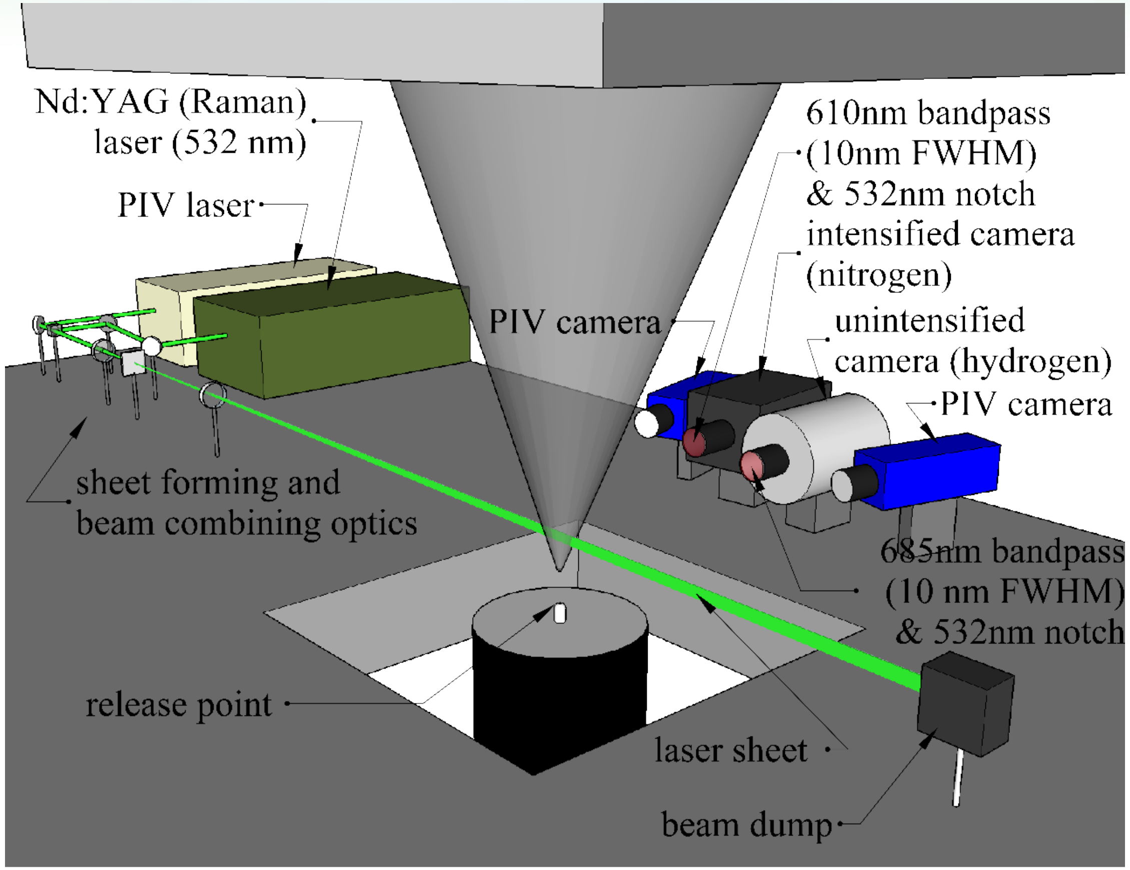
- Planar laser Rayleigh scattering used at Sandia for atmospheric temperature hydrogen releases
- Scatter proportional to number density; variations are caused by both composition and temperature
- For warm releases, always measured in atmospheric temperature region to eliminate this variable and enable composition quantification
- Not feasible to wait until cryogenic plume has warmed back to atmospheric temperature
- Rayleigh imaging will have signal overwhelmed by Mie scattering off of condensed entrained moisture in cryogenic plume
- Filtered Rayleigh has insufficient Mie scattering (condensed, entrained moisture) light suppression (OD≈3)



Planar Raman imaging works in a lab setting

H_2 Raman cross-section ≈ 10^{-30} cm^2

- Signals are low
  - High powered light source required (~700 mJ/pulse @ 532nm, 12mm tall sheet)
  - Fast optics for collection (F/1.2)
- Large Raman shift enables higher optical density filters to remove unwanted Mie scatter
  - 10 nm FWHM bandpass filters at wavelengths of interest
  - OD of 12 @ all wavelengths
  - OD of 18 @ 532 nm
- Signals for other Raman lines (rotational, etc.) low at cryogenic temperatures

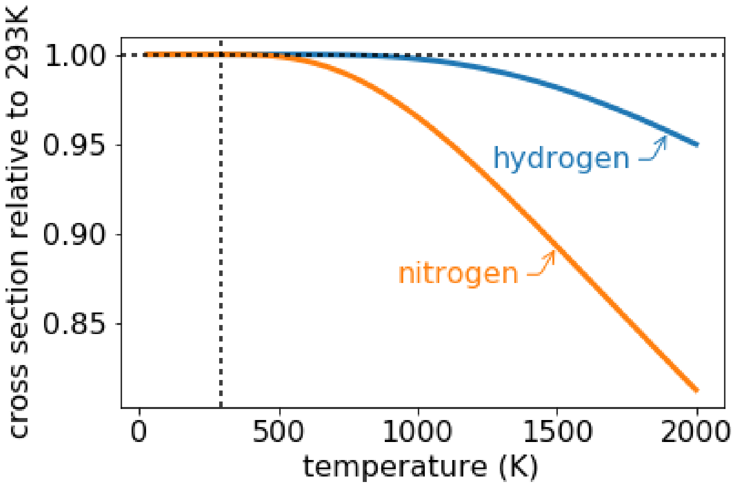


H_2: shift of 4161 cm^{-1} (532nm → 683 nm, 355nm → 416 nm)

N_2: shift of 2331 cm^{-1} (532nm → 607 nm, 355nm → 387 nm)

Quantification of Raman signals

- Signal is proportional to number density of molecules
- We use the ideal gas law to relate temperature and mole fraction to number density
  - $\frac{n_{total}\Sigma x}{V} = \frac{P_{total}\Sigma x}{RT}$
  - other equation of state could be used but may not have analytical solution
- Cross-section dependence matters for high-T (flames), but not low-T (cryogenic)



Eq. 1: $\frac{I_{H_2}}{I_0} = k_{H_2} \frac{x_{H_2}}{T}$ ← unknown 1, ← unknown 2

measured values

calibration constants

Eq. 2: $\frac{I_{N_2}}{I_0} = k_{N_2} \frac{x_{N_2}}{T}$ ← unknown 3

based on the composition of air

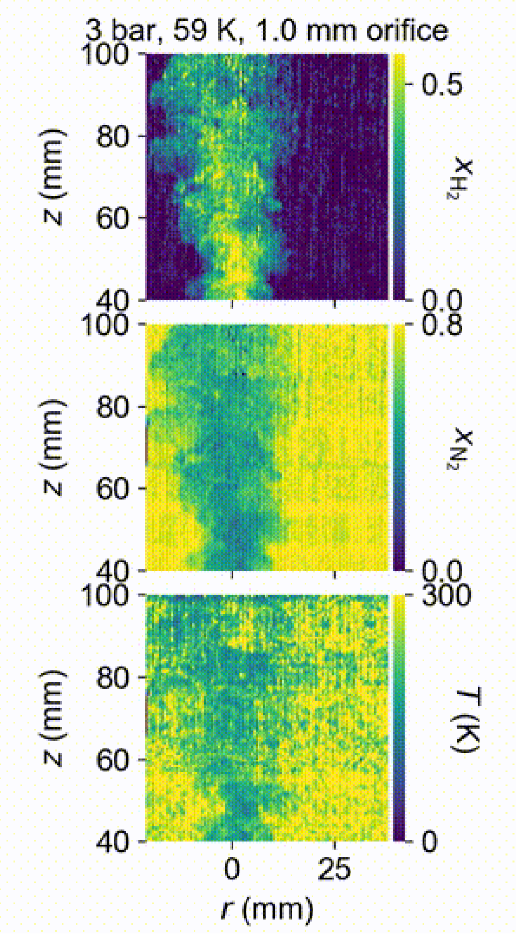
Eq. 3: $1 = x_{H_2} + 1.28 x_{N_2}$

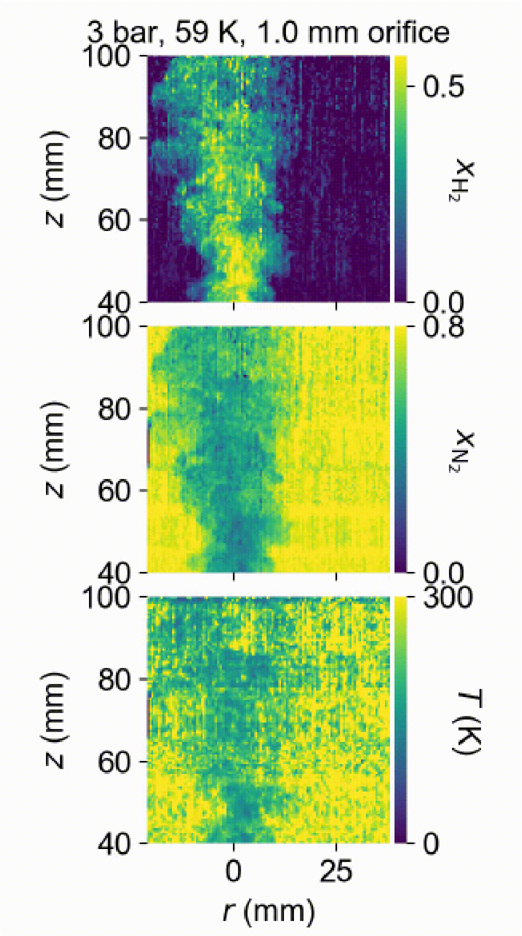
$$\begin{cases} x_{H_2} = \dfrac{\mathrm{I_{H_2}}}{k_{H_2}\left(\dfrac{\mathrm{I_{H_2}}}{k_{H_2}} + \dfrac{1.28\mathrm{I_{N_2}}}{k_{N_2}}\right)} \\ x_{N_2} = \dfrac{\mathrm{I_{N_2}}/\mathrm{I_0}}{k_{N_2}\left(\dfrac{\mathrm{I_{H_2}}}{k_{H_2}} + \dfrac{1.28\mathrm{I_{N_2}}}{k_{N_2}}\right)} \\ T = \dfrac{1}{\dfrac{\mathrm{I_{H_2}}}{k_{H_2}} + \dfrac{1.28\mathrm{I_{N_2}}}{k_{N_2}}} \end{cases}$$

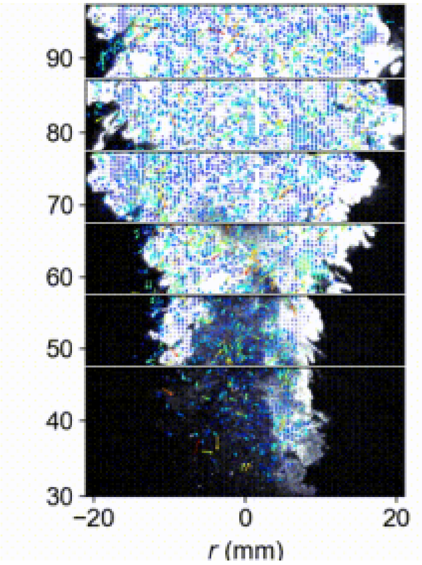
Raman has been used in a lab-scale campaign to measure releases from ≈1 mm orifices

T_{noz} [K]	P_{noz} [bar_{abs}]	d [mm]	T_{throat} [K]	n_{hts}
58	2	1	43.5	4
56	3	1	41.9	4
53	4	1	39.6	4
50	5	1	37.4	5
61	2	1.25	45.7	6
51	2.5	1.25	38.2	2
51	3	1.25	38.2	6
55	3.5	1.25	41.2	3
54	4	1.25	40.4	2
43	4	1	32.1	2
59	3	1	44.2	6
56	3.5	1	41.9	1
80	3	1	60.3	5

With PIV



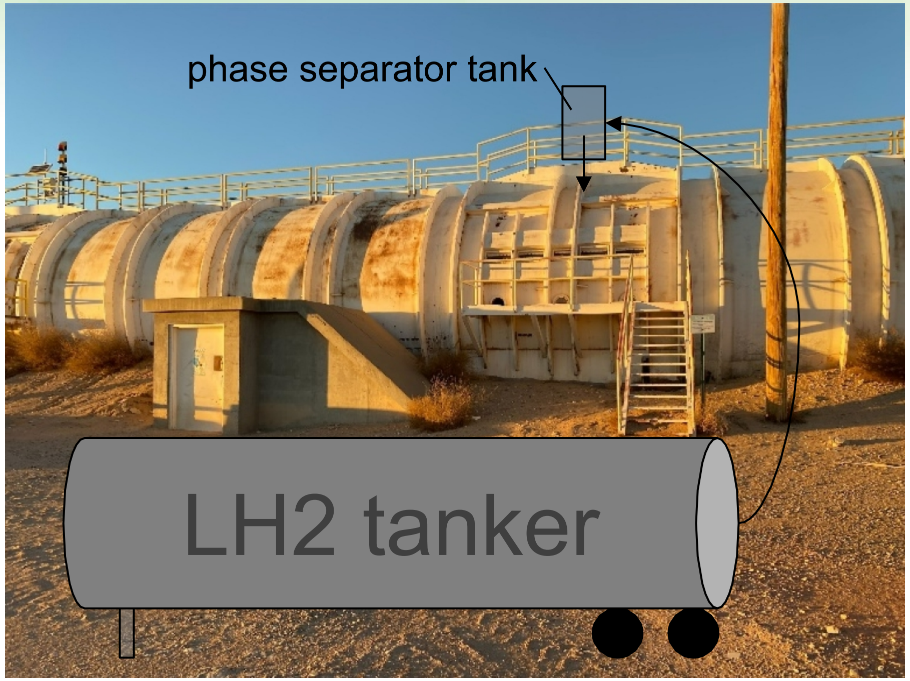


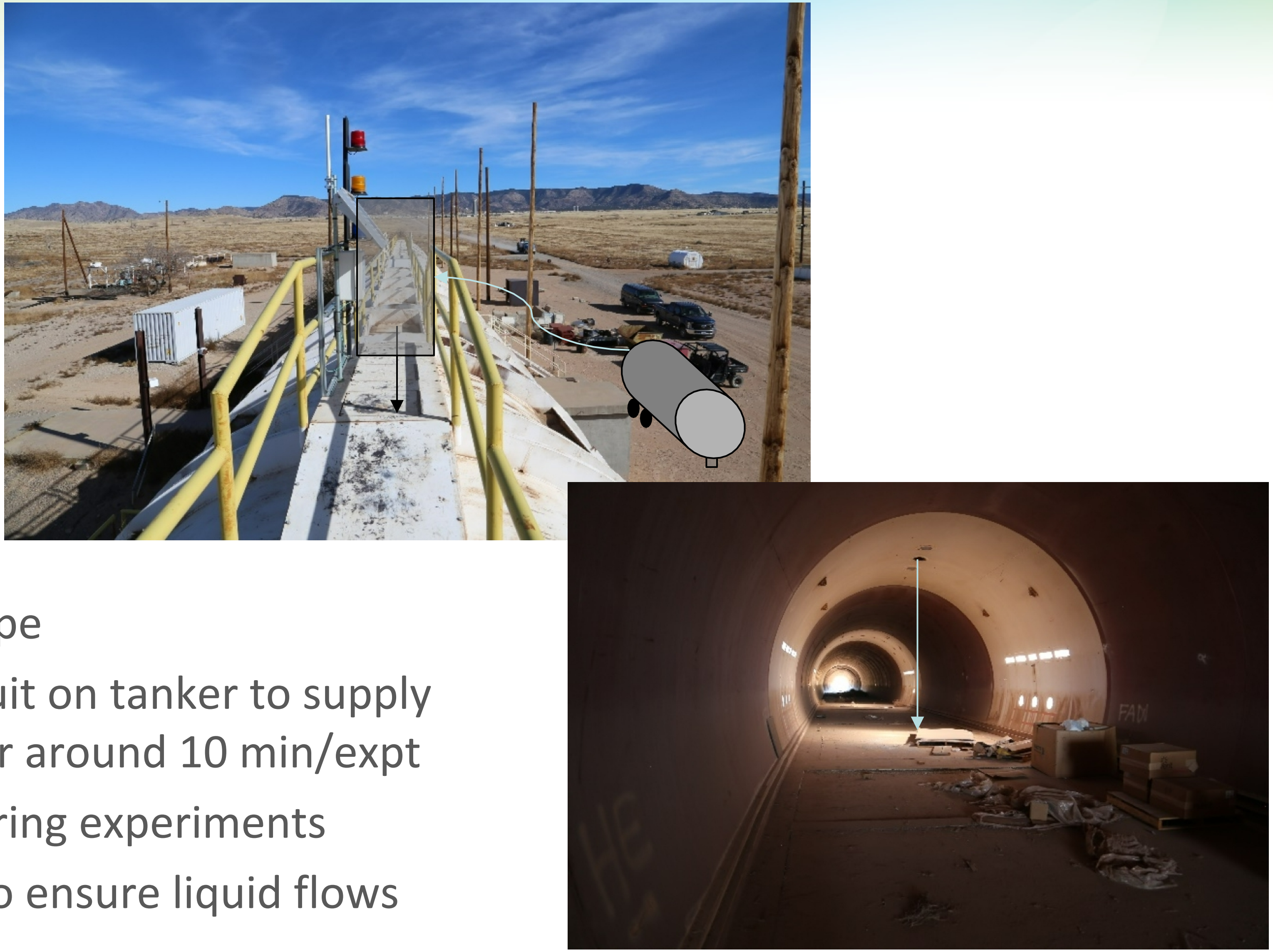


New experiments this FY will study pooling and vaporization

- Cryogenic vapor dispersion is reasonably well understood
- For larger breaches, pooling may occur and vaporization from this pool provides a source term for cold vapor dispersion
- Validation data is needed for pooling, vaporization, and dispersion from pools in a crosswind
- Well-controlled experiments are being planned
  - In Sandia's Thunderpipe
  - Variations in cross-wind, LH2 release rate, and surface

We are working with vendors to set-up the experiments





- LH2 tanker to sit outside thunderpipe
- Use valving and pressure build circuit on tanker to supply steady flow of LH2, 10-100 l/min for around 10 min/expt
- Flow system remotely operated during experiments
- Phase separator near experiment to ensure liquid flows