Mid IR Laser Sensor for Continuous SO_3 Monitoring to Improve Coal-Fired Power Plant Performance during Flexible Operations

Contract# FE-0031560

Period of Performance: 03/30/2018 to 01/31/2022

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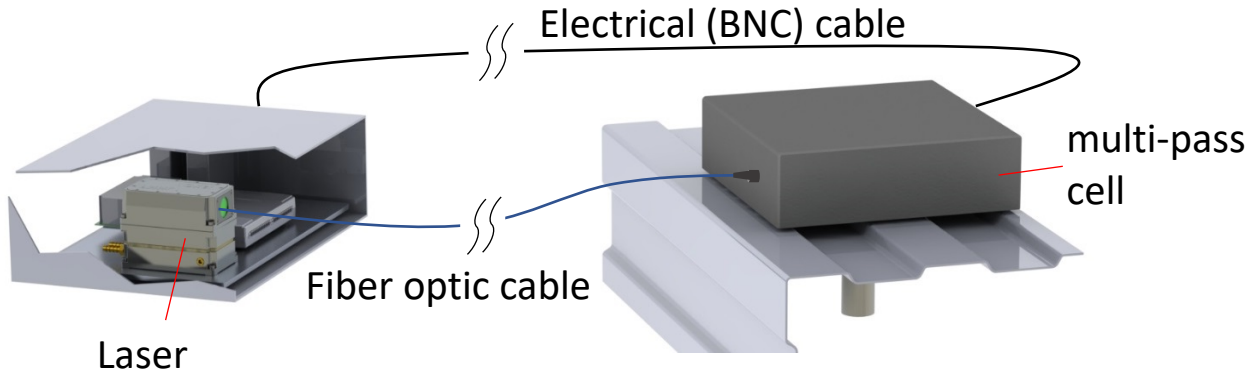
Project Description and Objectives

Purpose:

- Produce and demonstrate a continuous SO_3 / H_2SO_4 monitor for coal-fired power plants

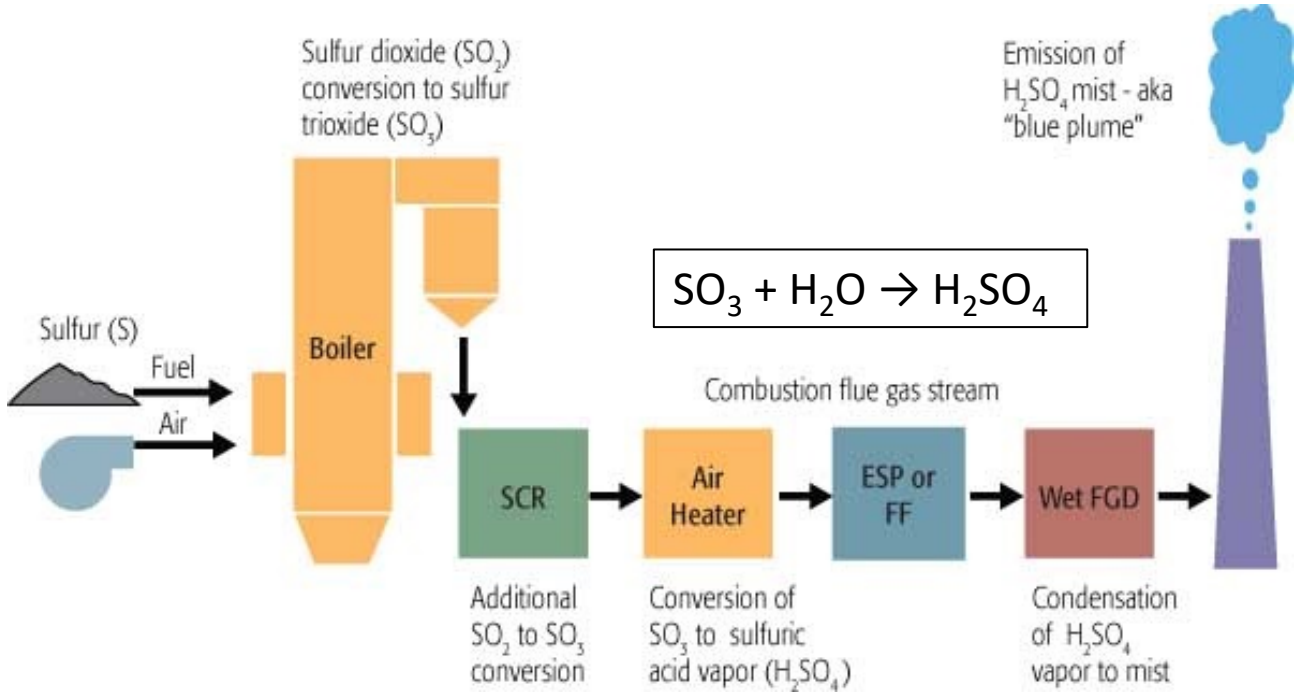


Alignment to Fossil Energy objectives

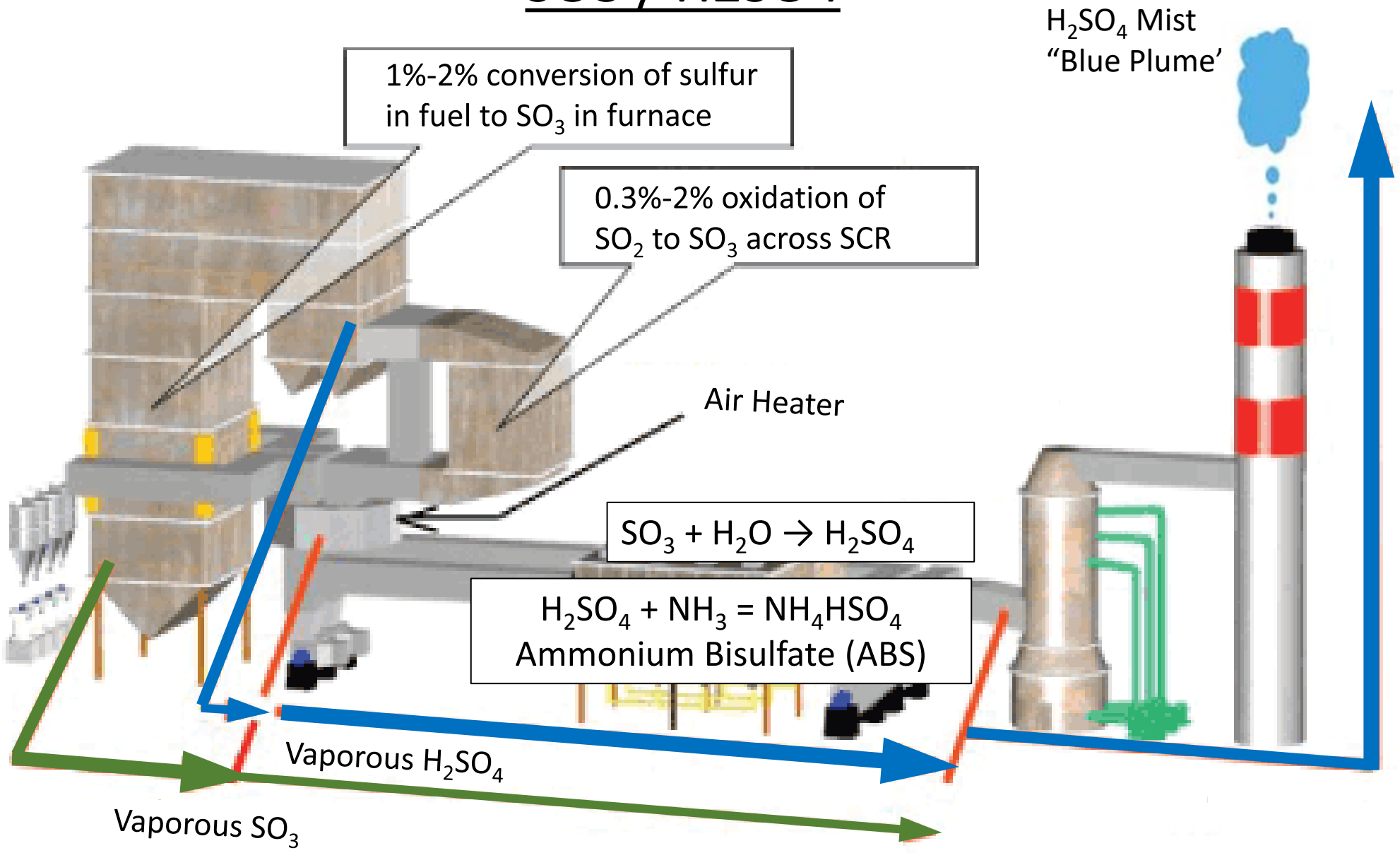
- Real-time information to optimize additive injection and minimize catalyst deactivation
- Without an SO_3 monitor, power plants over use sorbent => waste (typical sorbent costs $1M/yr)
- Sensor would enable cost savings ($100k/yr – $200k/yr) and improved flexible operations

Driving questions

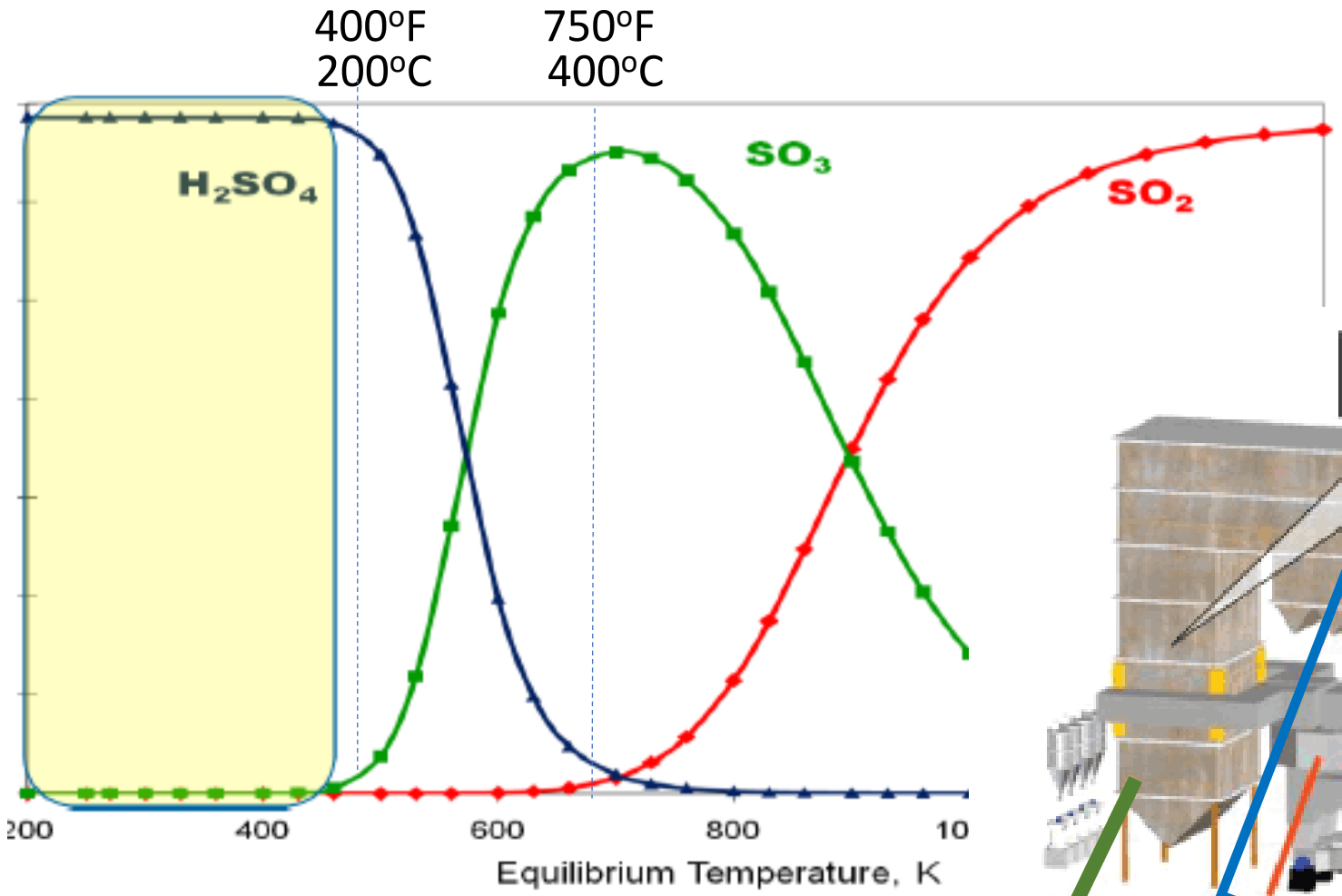
- Can the sensor provide sufficient sensitivity in a challenging environment?
- Do measurements accurately reflect the composition of the flue gas?

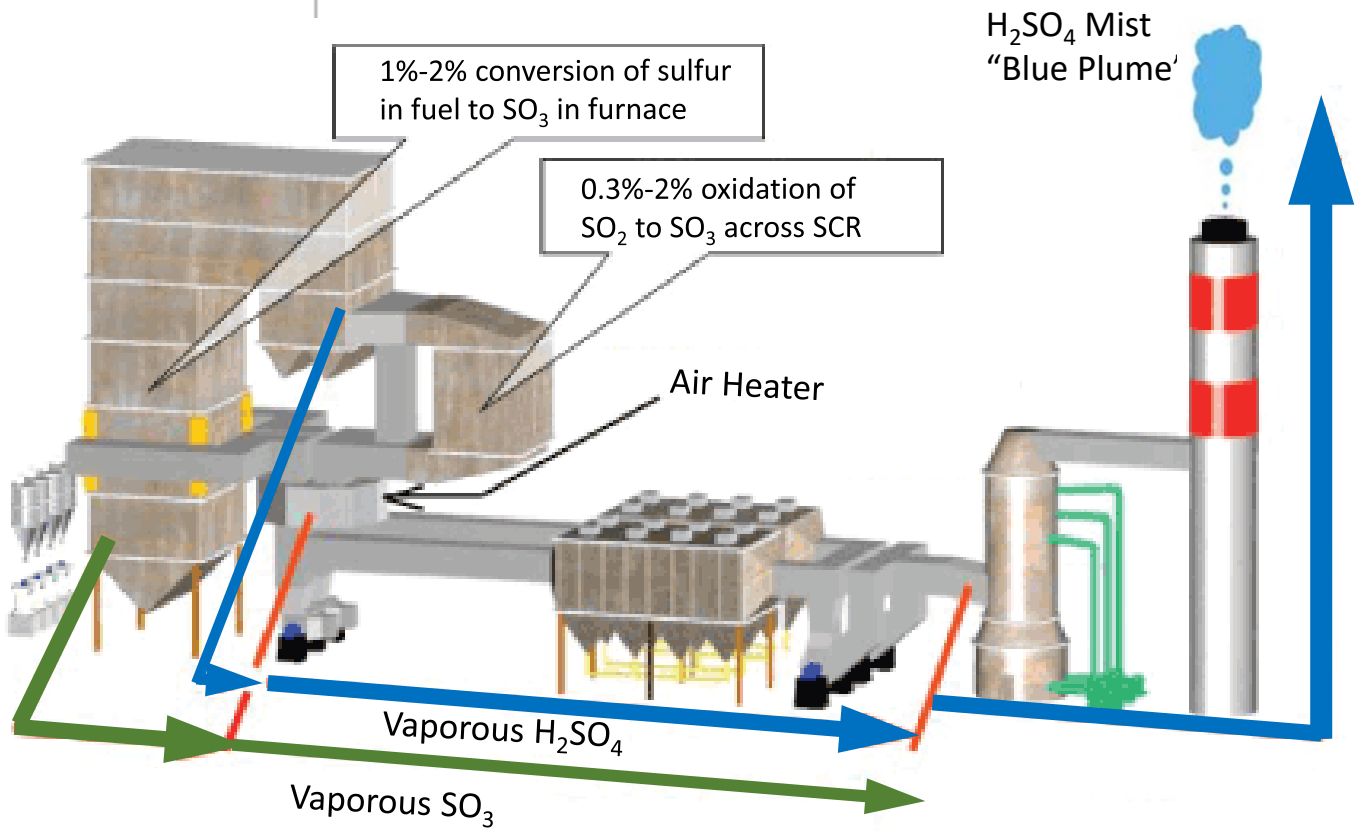


SO3 / H2SO4


H_2SO_4 Mist
"Blue Plume'
1%-2% conversion of sulfur in fuel to SO_3 in furnace
0.3%-2% oxidation of SO_2 to SO_3 across SCR
Air Heater
$SO_3 + H_2O \rightarrow H_2SO_4$
$H_2SO_4 + NH_3 = NH_4HSO_4$
Ammonium Bisulfate (ABS)
Vaporous H_2SO_4
Vaporous SO_3

Equilibrium Conditions vs Temperature





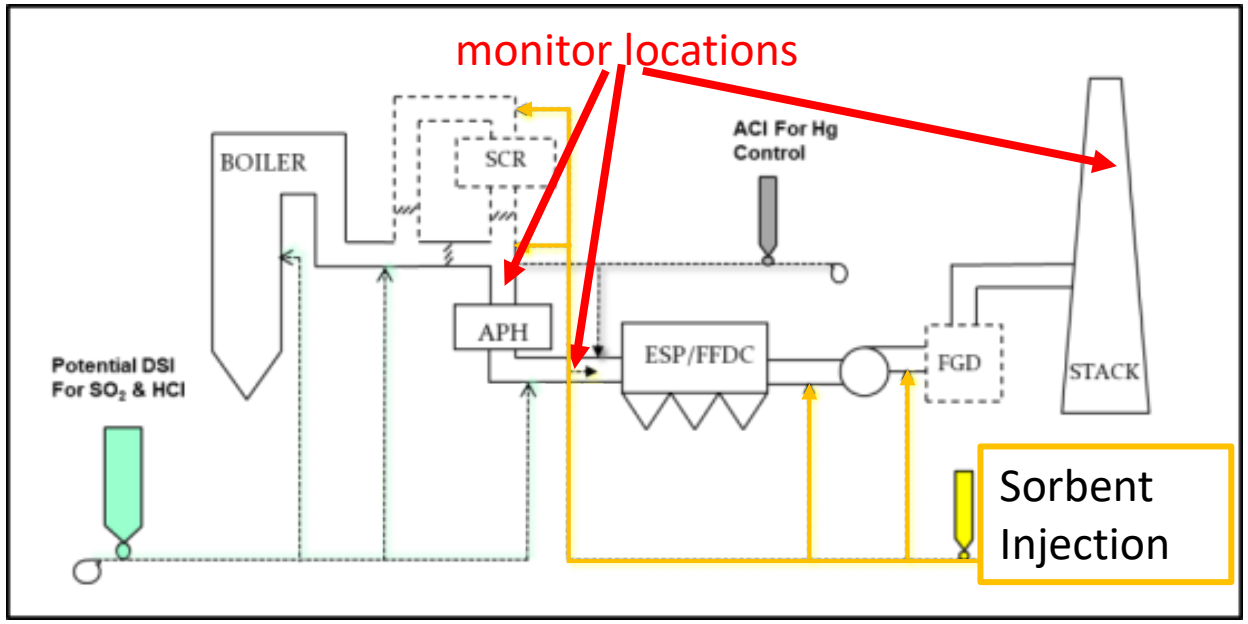
$SO_3 + H_2O \rightarrow H_2SO_4$

$H_2SO_4 + NH_3 = NH_4HSO_4$ Ammonium Bisulfate (ABS)

Alkali Sorbent Injection

Alkali sorbent injection uses include:

- Mitigation of H_2SO_4 'blue plume'
- Enhanced powdered activated carbon (PAC) efficiency in capturing mercury
- Mitigation of ammonium bisulfate (ABS) and SO_3 condensation impacts on air heater fouling
- Mitigation of duct corrosion due to SO_3 condensation

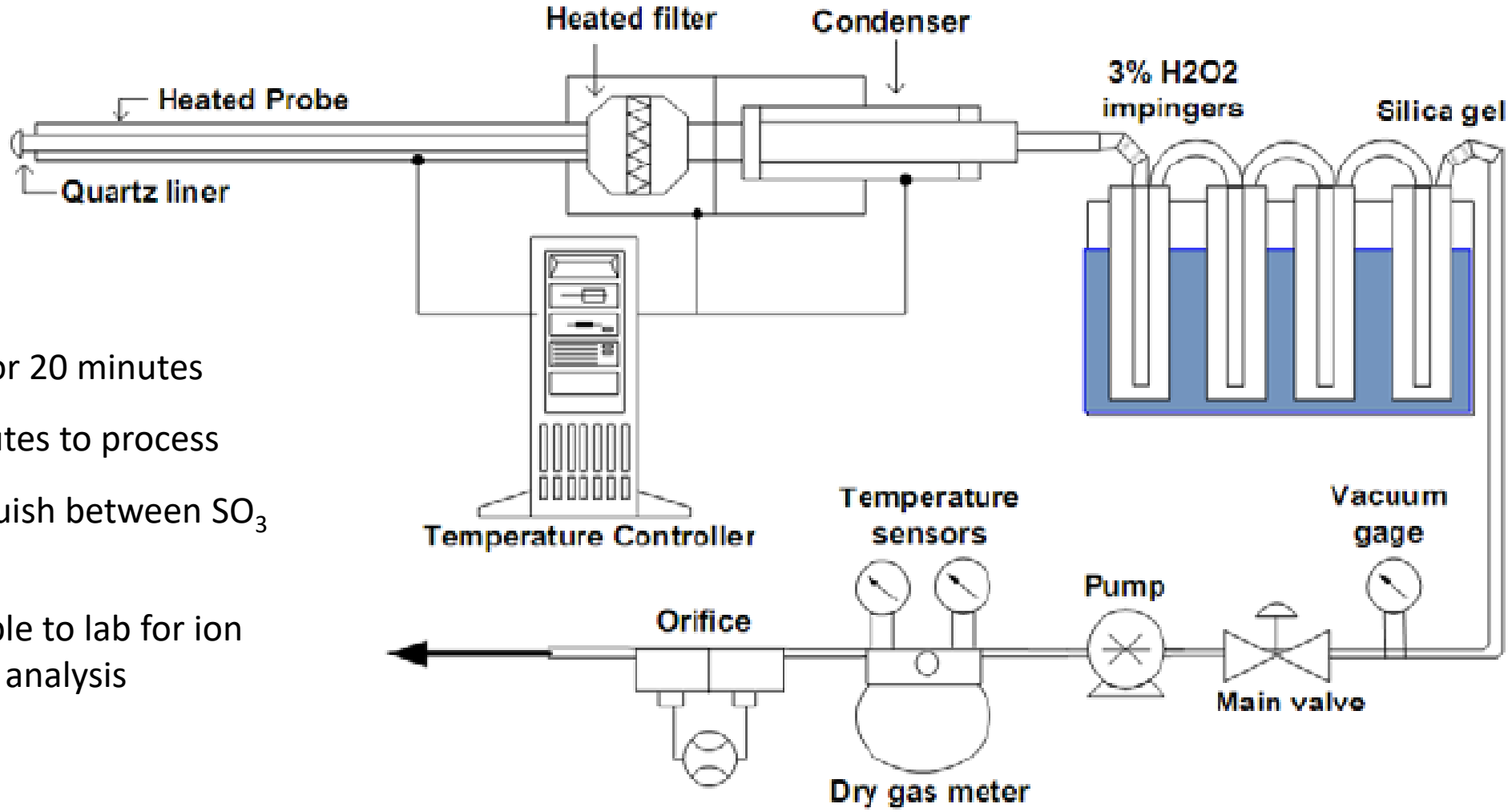


Alkali sorbent injection locations moving upstream:

- Originally downstream of air heater / upstream of particulate collection device
- Also between the Selective Catalytic Reduction (SCR) outlet and air heater
- Recently positioned upstream of the SCR

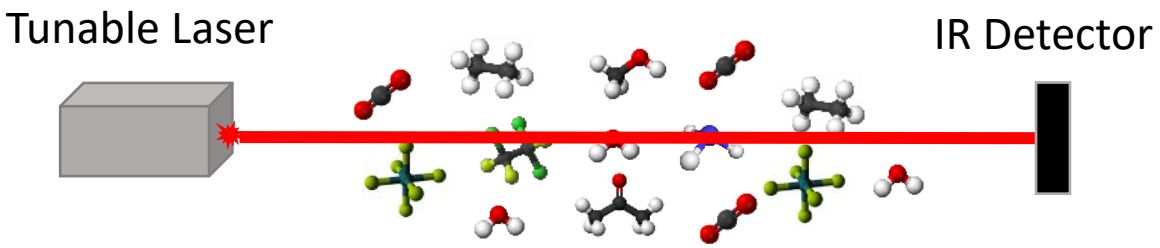
Lack of continuous SO_3 monitor limits ability to optimize sorbent injection rates

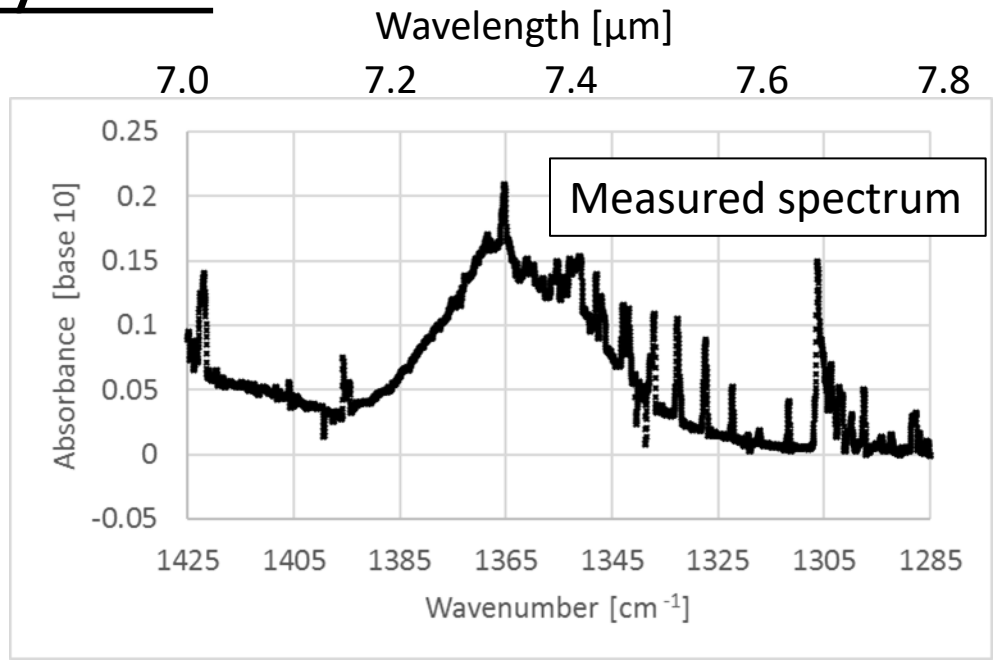
Current Technique for SO3 / H2SO4

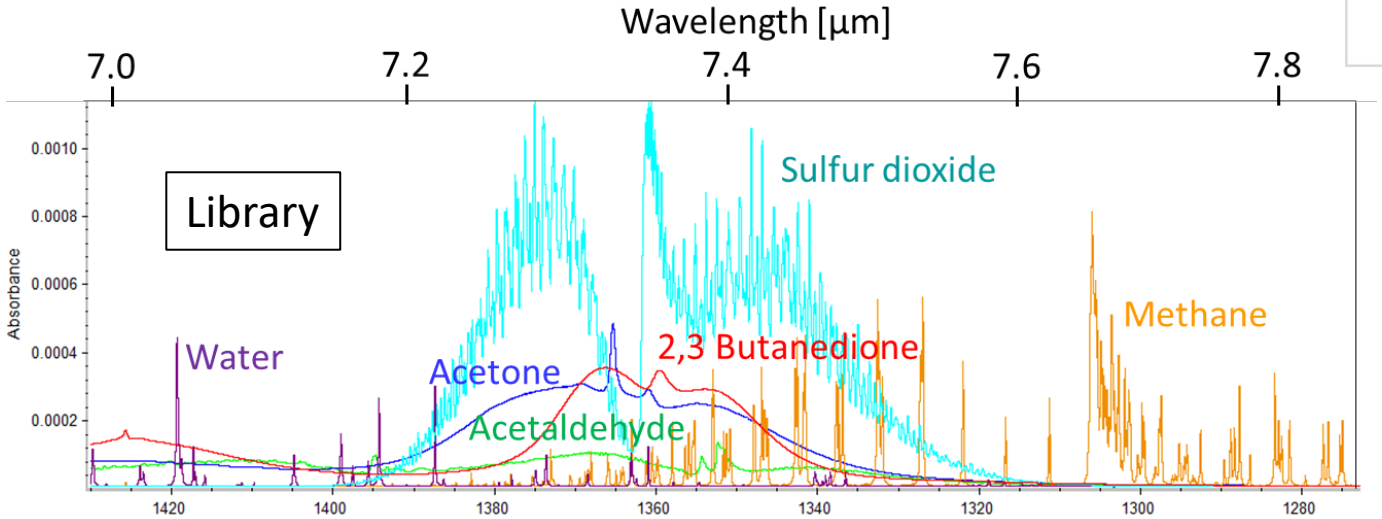


- Collect sample for 20 minutes
- Another 20 minutes to process
- Does not distinguish between SO_3 and H_2SO_4
- Send liquid sample to lab for ion chromatography analysis

Spectroscopy System







Species Concentration

2,3 Butanedione:	99.7 ppm
Acetaldehyde:	230.2 ppm
Acetone:	130.8 ppm
Methane:	259.3 ppm
Water:	-38.8 ppm
Sulfur dioxide:	2.5 ppm

H2SO4 Spectrum

Vibrational and Electronic Spectroscopy of Sulfuric Acid Vapor

Paul E. Hintze, Henrik G. Kjaergaard, Veronica Vaida, and James B. Burkholder

The Journal of Physical Chemistry A **2003** *107* (8), 1112-1118
DOI: 10.1021/jp0263626

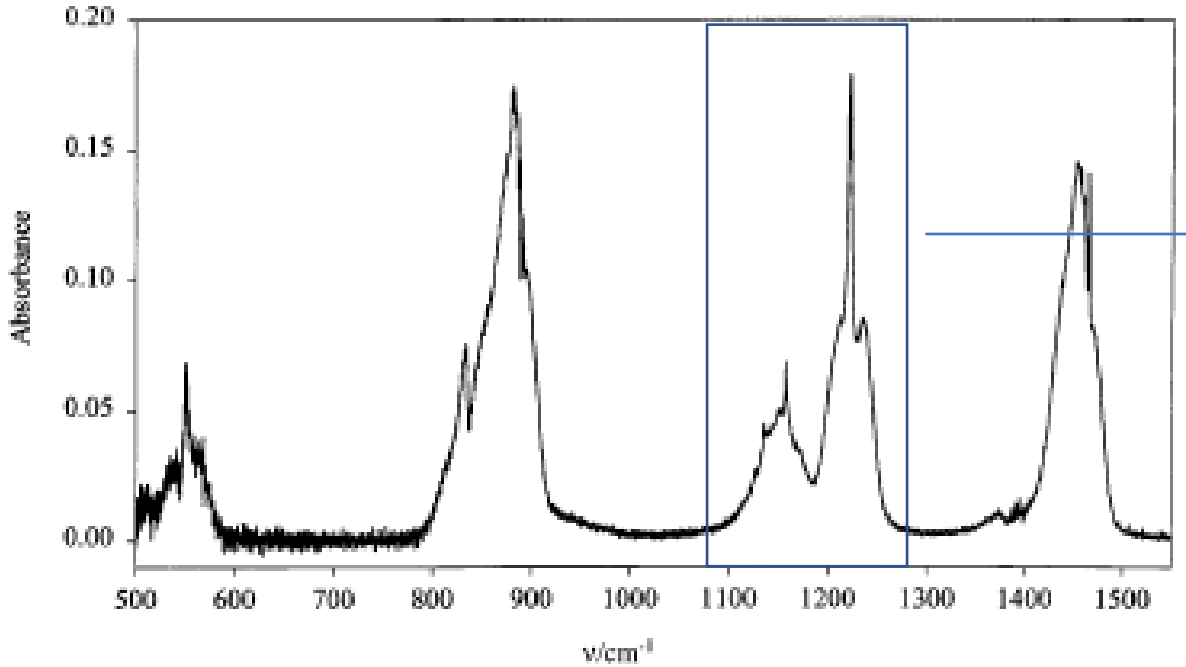
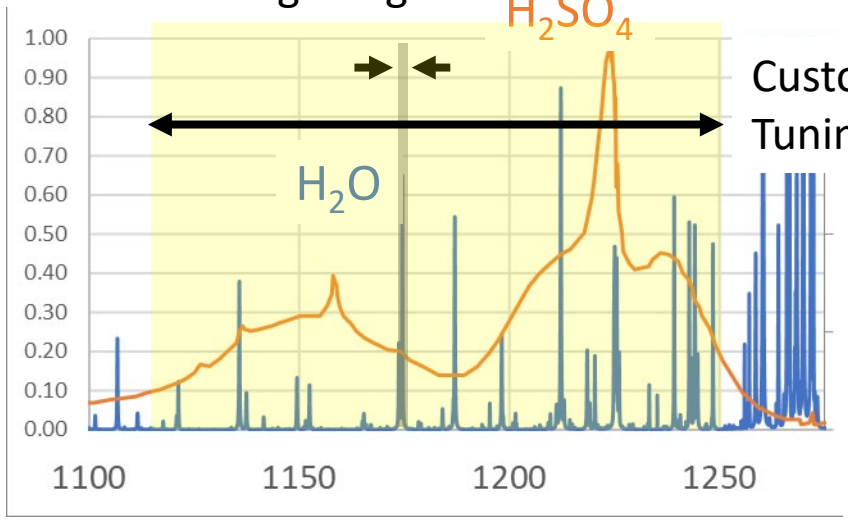


Figure 1. Vapor-phase IR spectrum of H_2SO_4 in the range of 500–1550 cm^{-1}. The spectrum was recorded at 150 °C with a path length of 100 cm. The reference spectra of H_2O and SO_3 have been subtracted.

H_2SO_4 Absorption Spectrum is not well characterized

Standard Laser Tuning Range



Custom Laser Tuning Range

Wavenumbers [cm^{-1}]

H_2SO_4 spectrum is broad

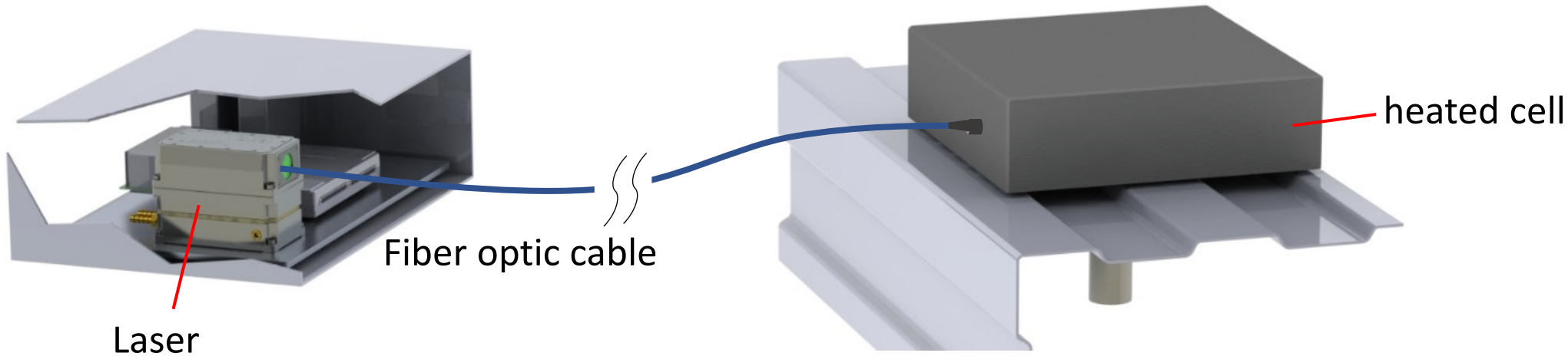
System Innovations

- Extractive measurements are not representative
- Cross-duct measurements suffer from alignment and transmission issues (soot)
- Absorption features strongest in Mid-IR
- Absorption feature are relatively broad spectrally
- Lasers should be remotely located from hot cell

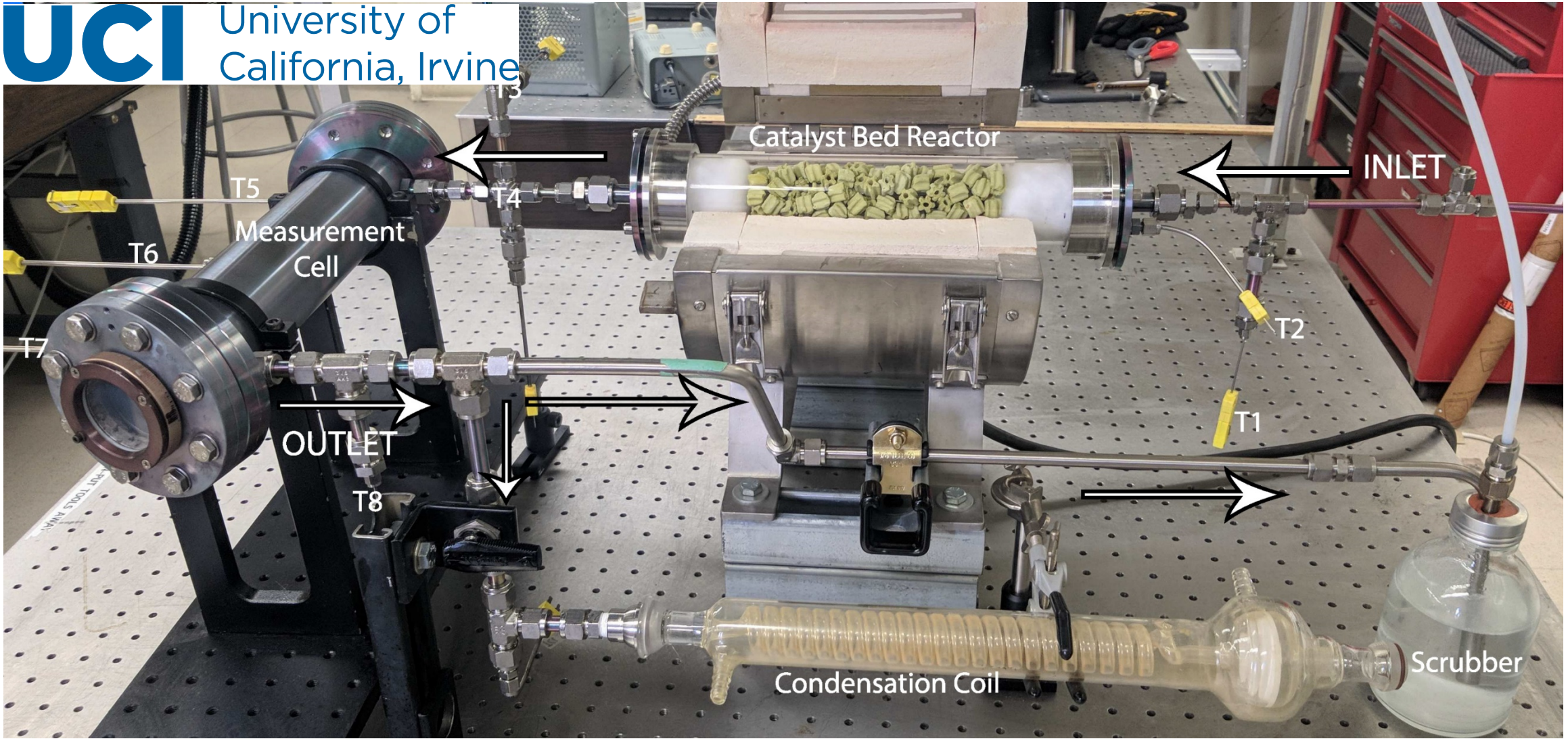
→ Heated, close-coupled multi-pass cell

→ Custom, broad-tuning Mid-IR lasers

→ Proprietary, hollow-core fiber optics



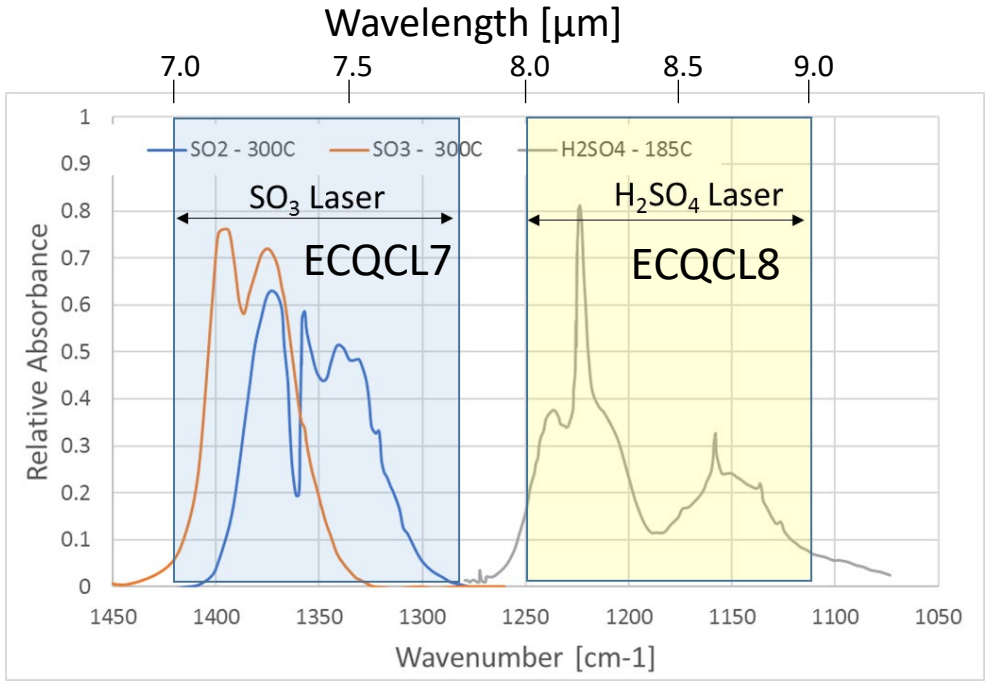
Lab-based Flue Gas Test Facility

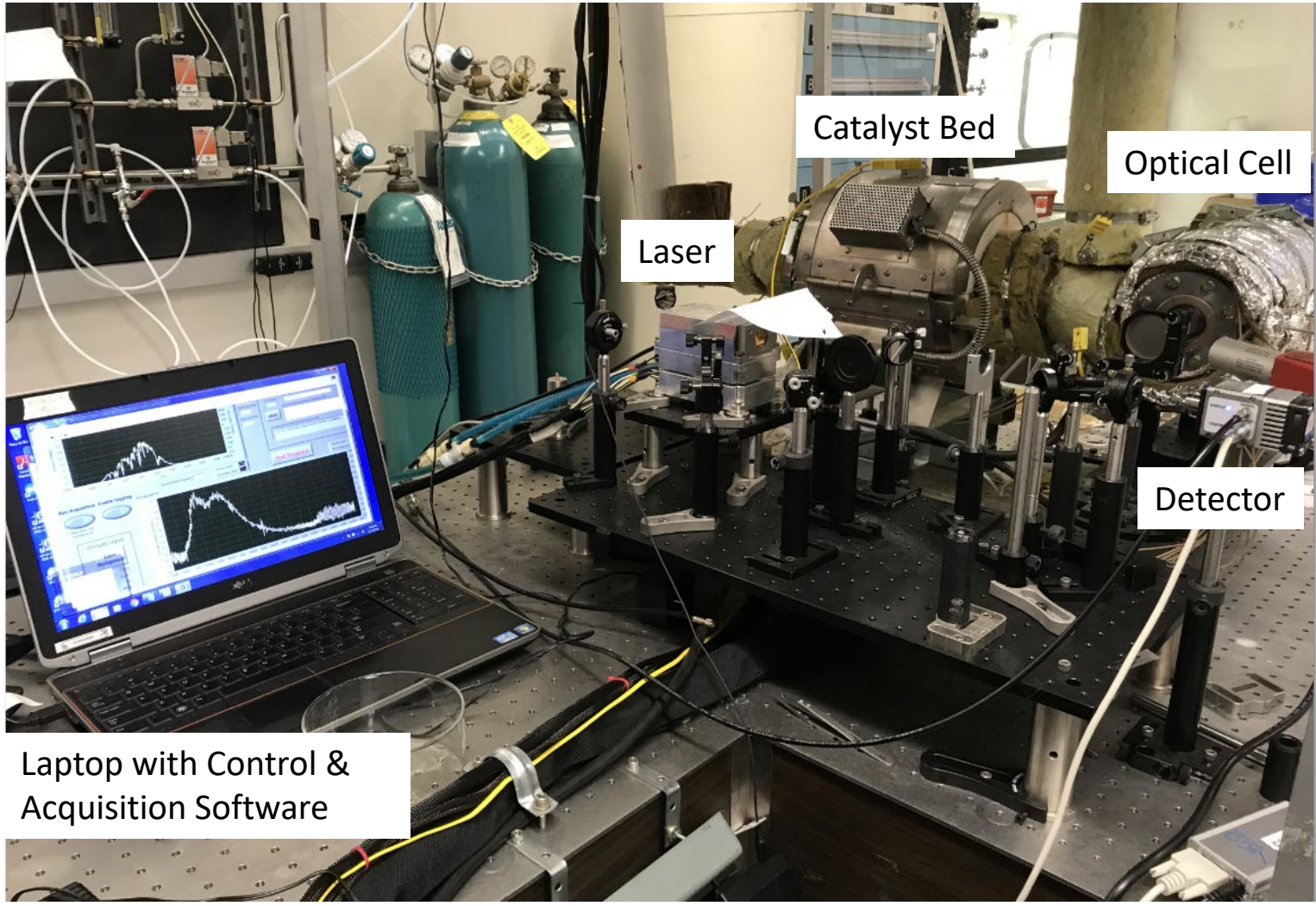


Lab Testing

UCI University of California, Irvine

- Controlled conditions with ability to vary: SO_2, SO_3/H_2SO_4, H_2O, Temperature
- Generate “library spectra”





Higher Fidelity Testing

FERCo
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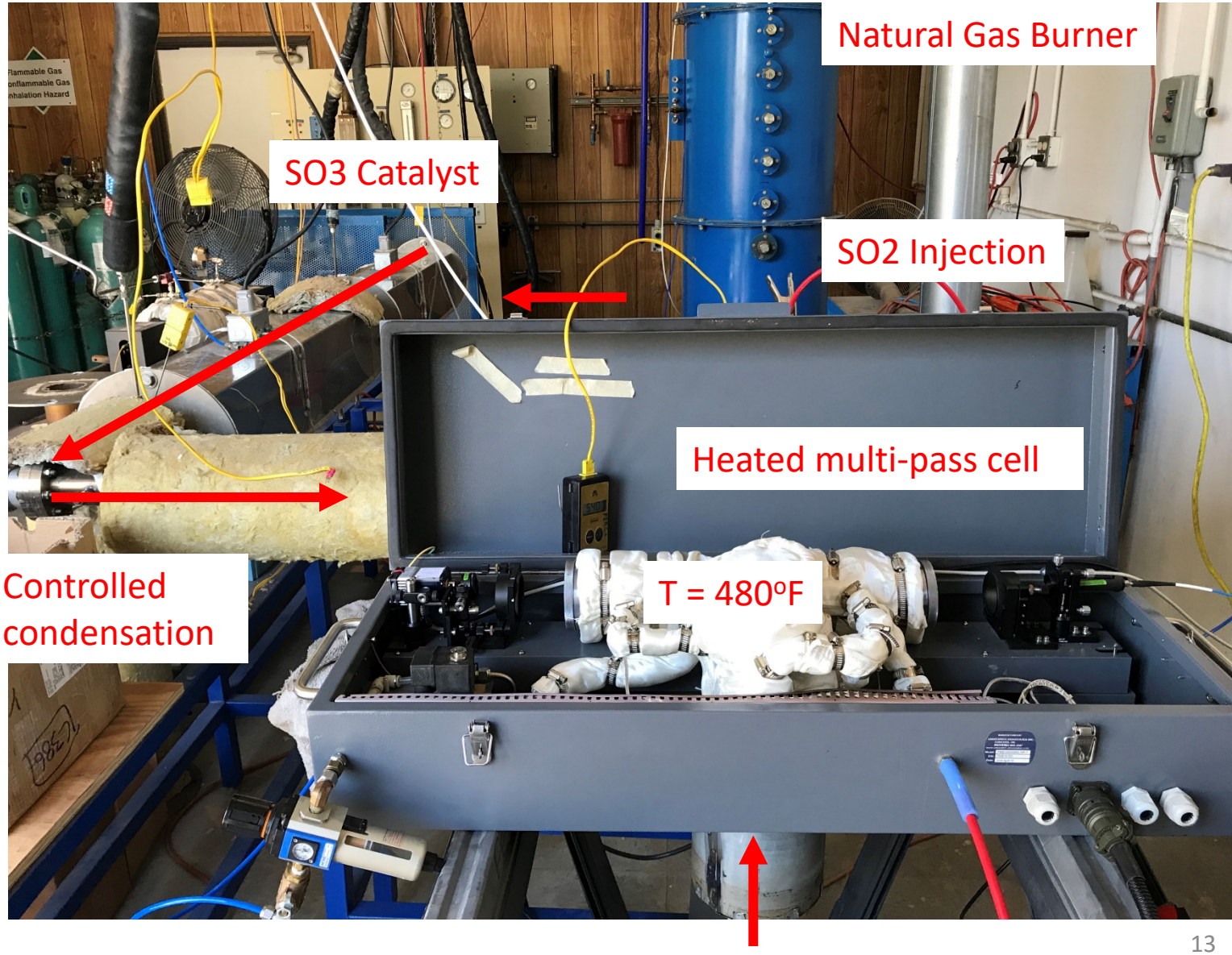
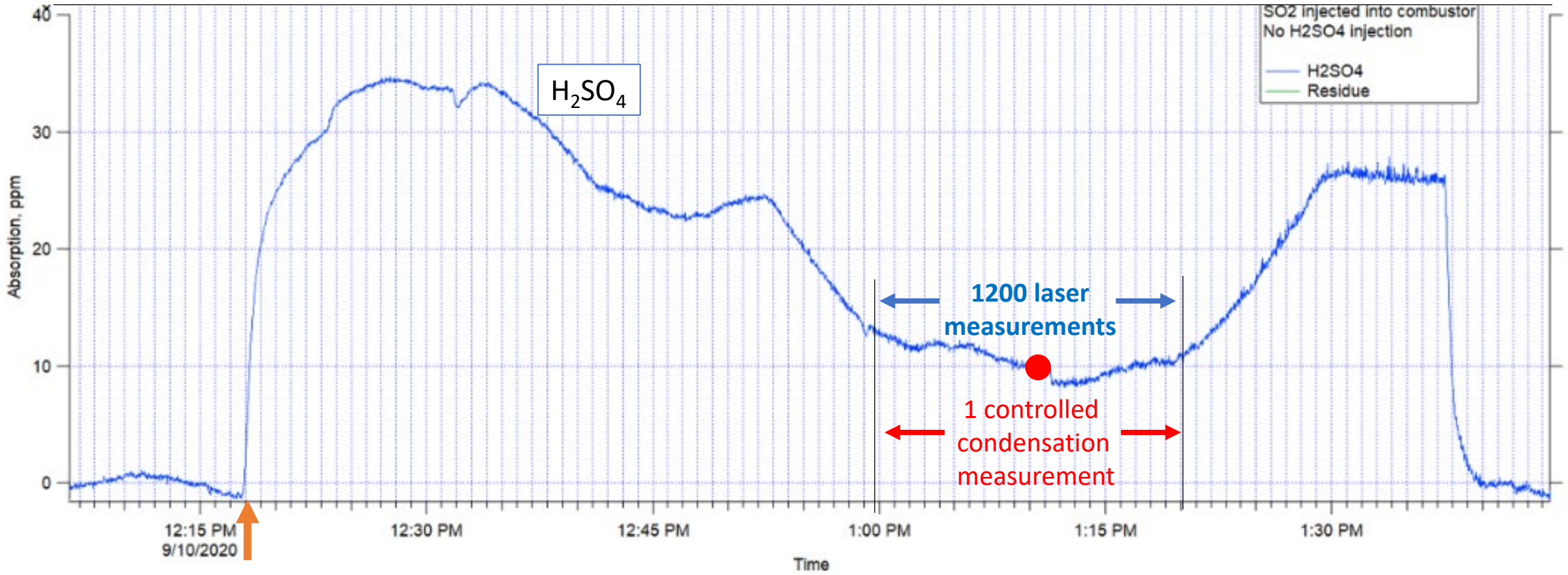
- Industrial facility for catalyst testing
- Hot flue gas with ability to add SO_2 and generate SO_3 / H_2SO_4
- Controlled condensation performed and utilized as “ground truth”
- SO_3 difficult to measure in presence of high SO_2 concentration

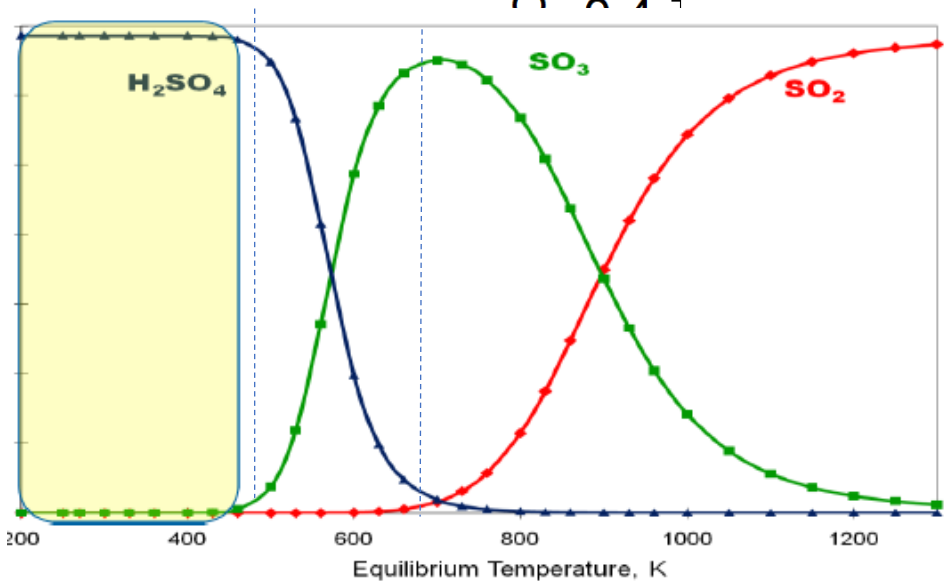


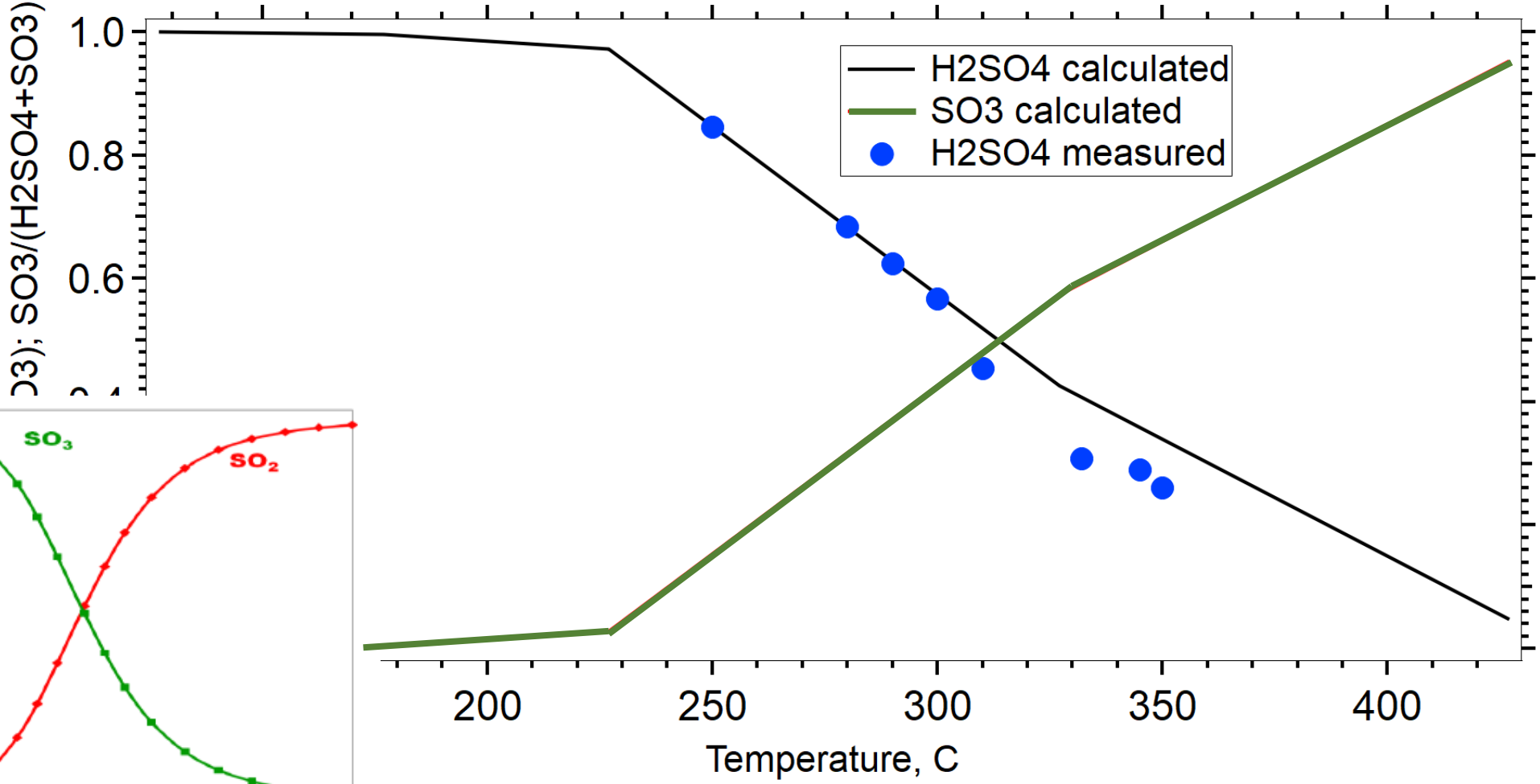
Real-time H2SO4 Measurements

- Laser measurements, real-time updated every second (1 Hz) – can observe dynamics
- Laser measurement precision better than 1 ppm at 1 Hz – better precision possible with averaging



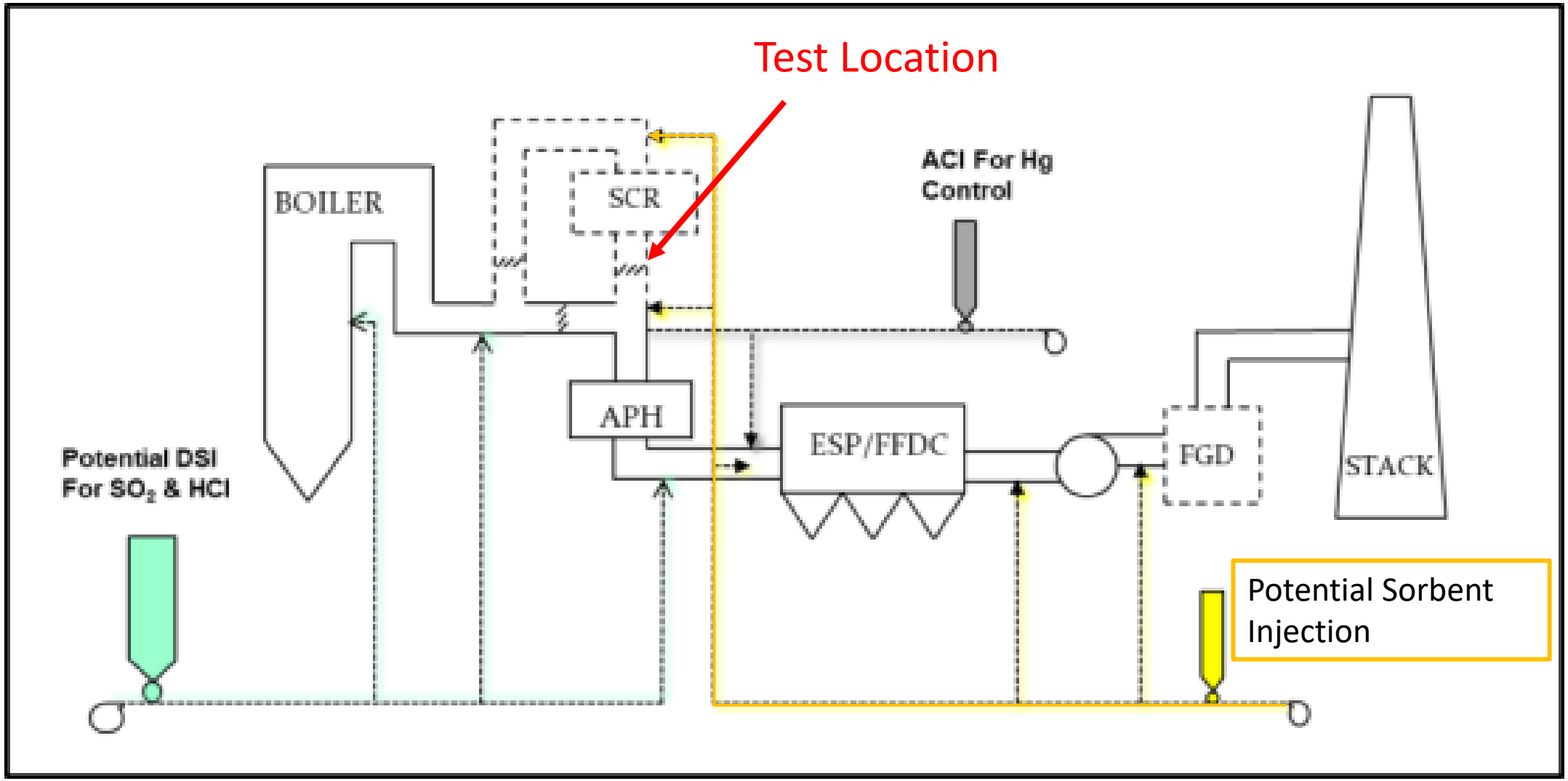
H2SO4 Measurements Vs. Cell Temperature





Power Plant Test Site

Measure at Output of SCR



Parallel Measurements

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- Site coordination / test management

optoknowledge

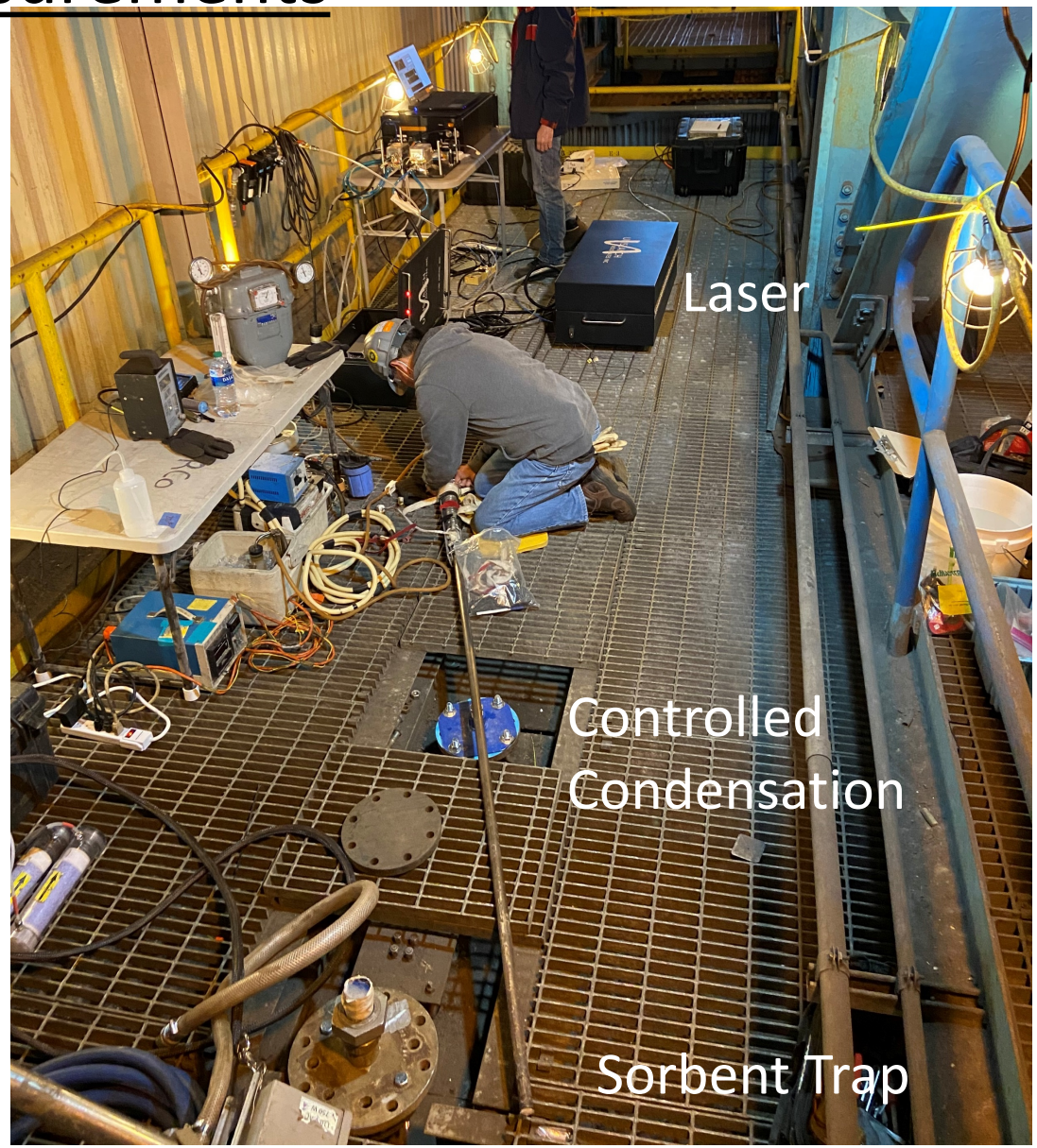
- Laser (H_2SO_4, SO_2, H_2O)

FERCo FOSSIL ENERGY RESEARCH CORPORATION

- Controlled condensate wet chemical measurements (SO_3 + H_2SO_4)

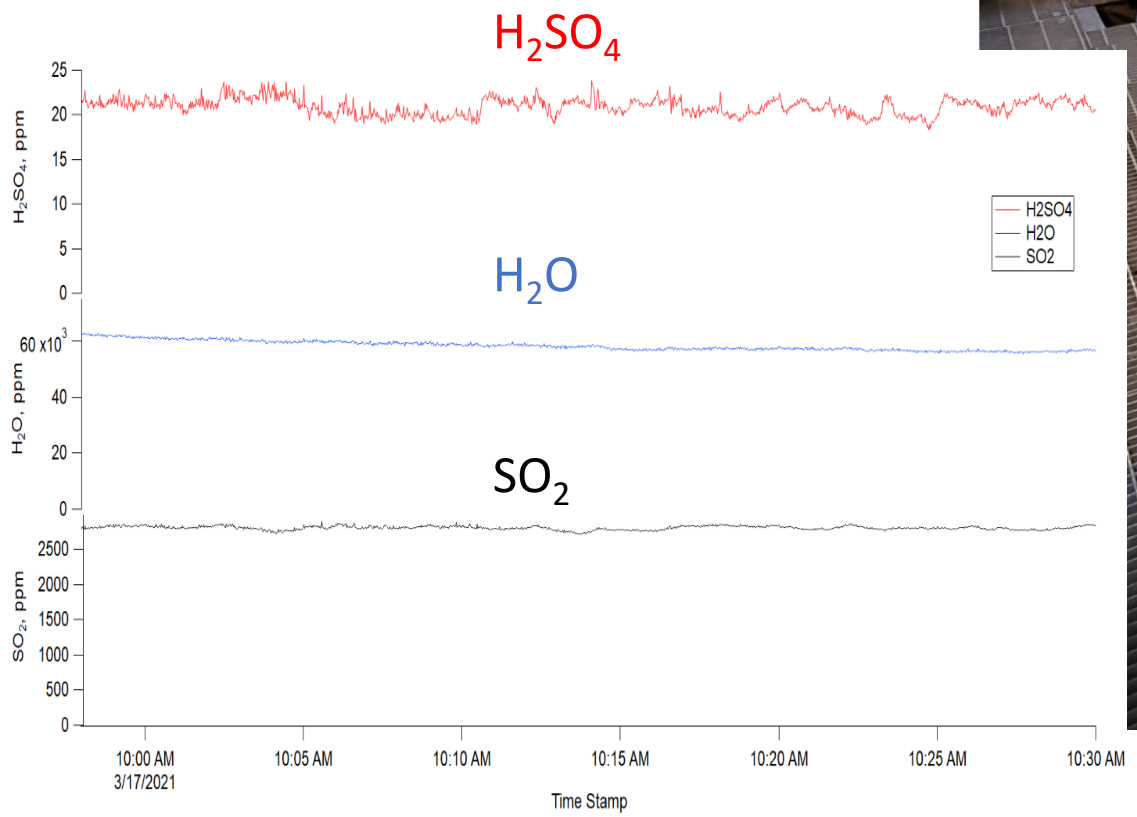
OHIO LUMEX

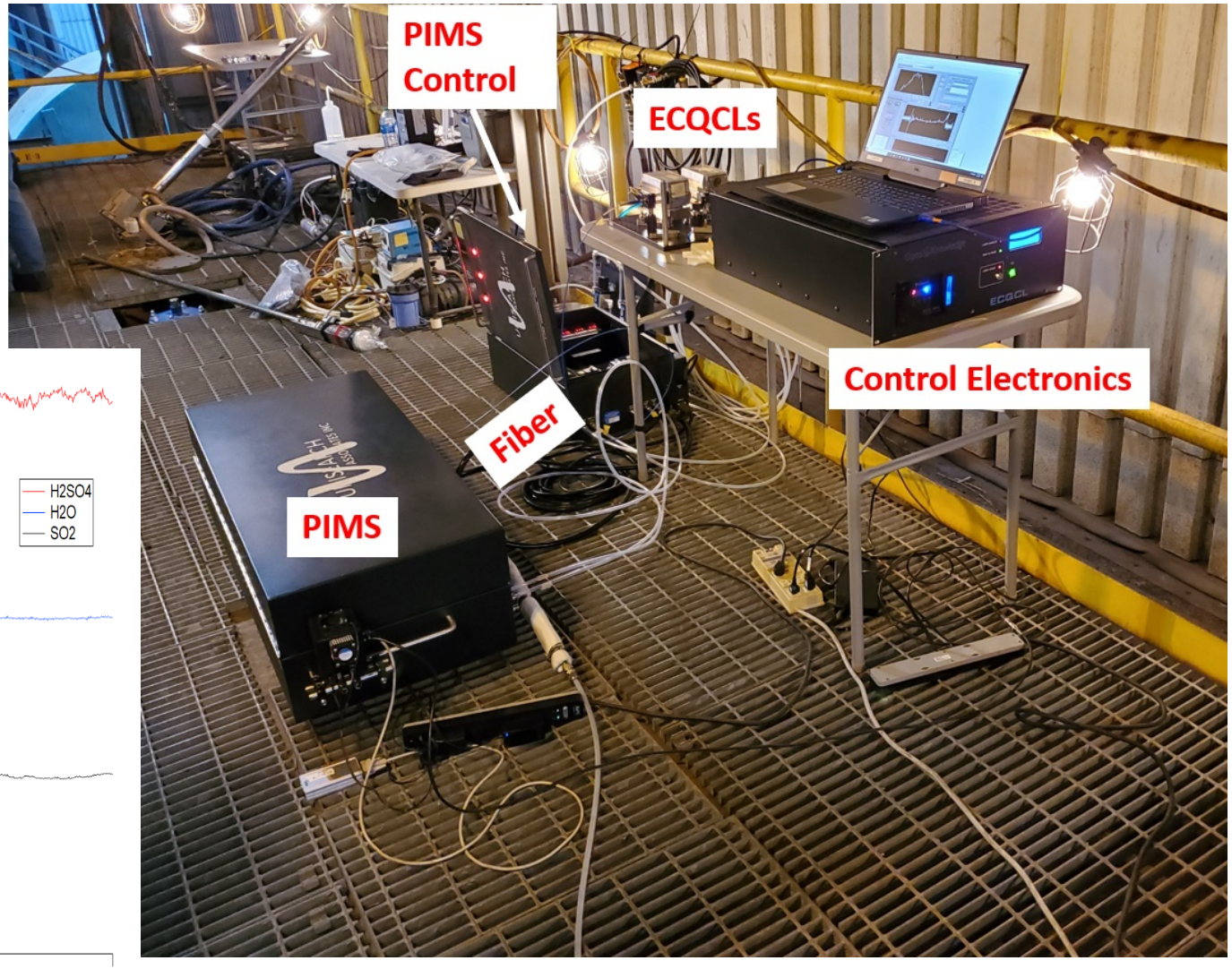
- Sorbent trap measurements (SO_3 + H_2SO_4)



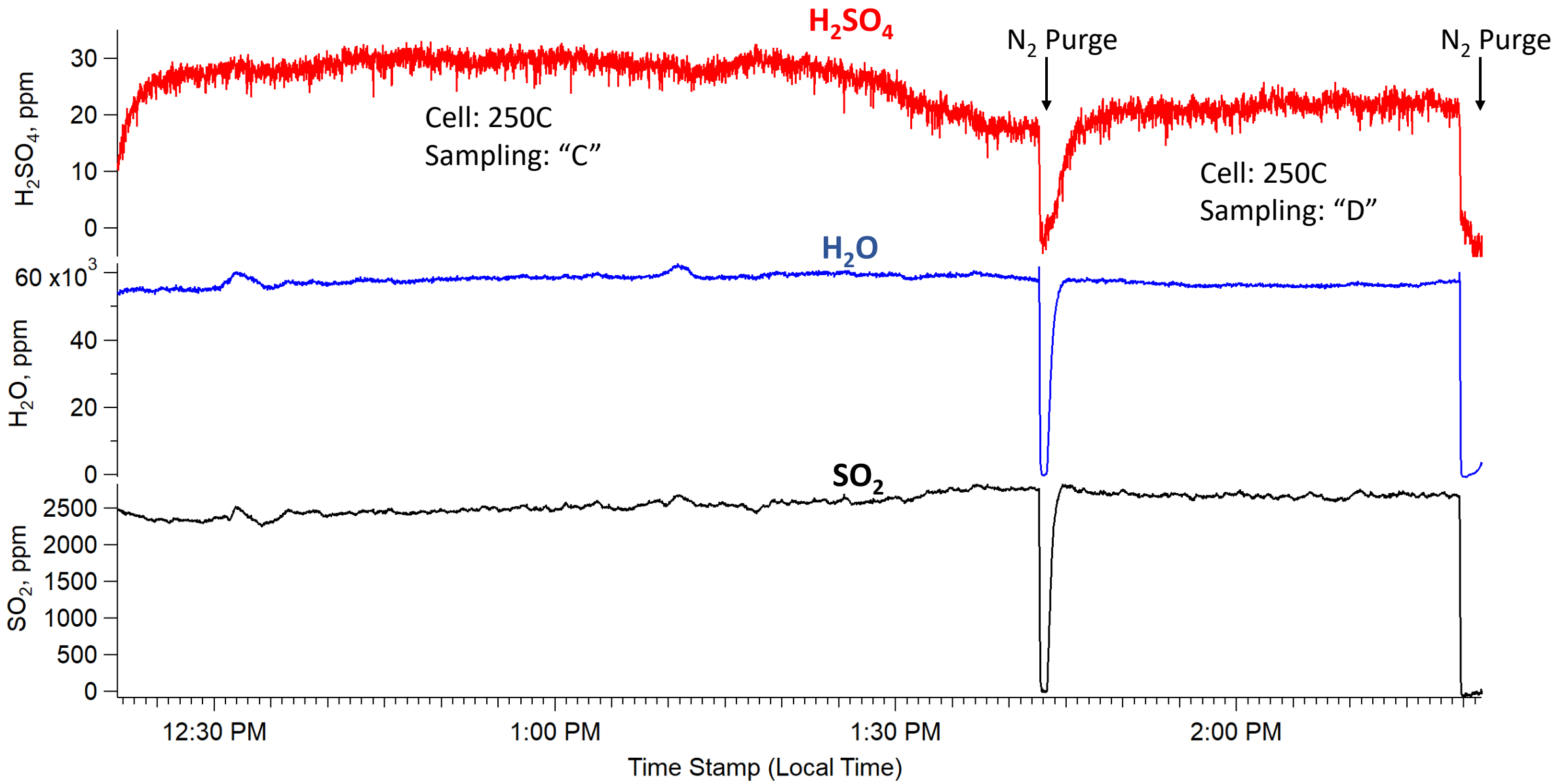
Laser Measurements

- Real time concentration 1 second update
- Tried two different probes
- Conducted tests at different cell temperatures





Laser Measurements



Measurement Comparison

Date	Load	Sampling Setup	Laser Cell Temp	H2SO4 [ppm]	Total: H2SO4 + SO3 [ppm]			SO2 [ppm]		H2O [%]	
				Laser	Laser	C.C.	Trap	Laser	Calc.	Laser	Calc
3/16	700	A	300 C	0.59	1	42	36	2944	2979	7.6	7.03
	700	A	250 C	5.5	7	41	34	2985	2979	7.8*	7.03
3/17	650	B	250 C	16	21	46	44	2795	2940	6.8*	6.77
	650	B	300 C	10	21	45	42	2717	2940	6.8	6.77
3/18	545	C	250 C	24	35	54	47	2433	2663	6.8*	6.23
	545	C	250 C	25	36			2470	2663	6.7*	6.23
	545	C	250 C	25	37			2447	2663	6.8*	6.23
	545	C	250 C	28	41			2366	2663	6.9*	6.23
	625	C	250 C	30	42			2527		7.3*	6.57
	650	D	250 C	23	32			2600		7.3*	6.77
	650	E	250 C	22	29			2699		7.0*	6.77

* H2O measurements with cell at 250 C using library at 300 C are adjusted by a scaling factor

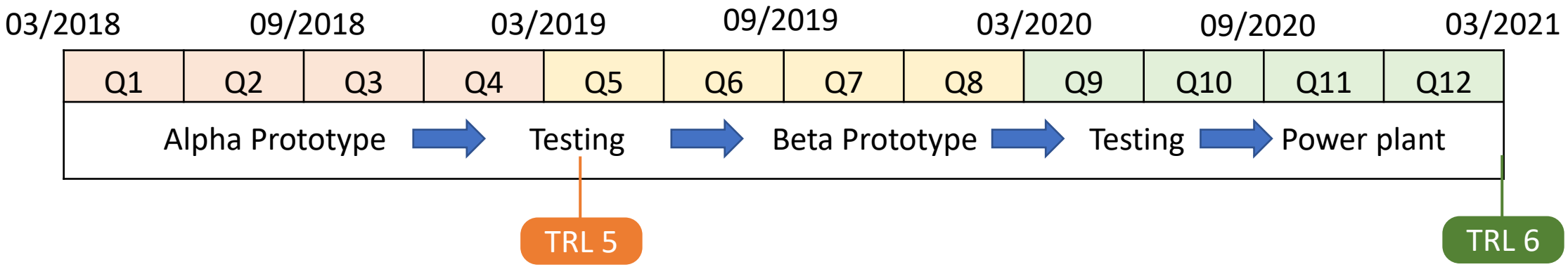
Project Overview and Status

Overview of Project

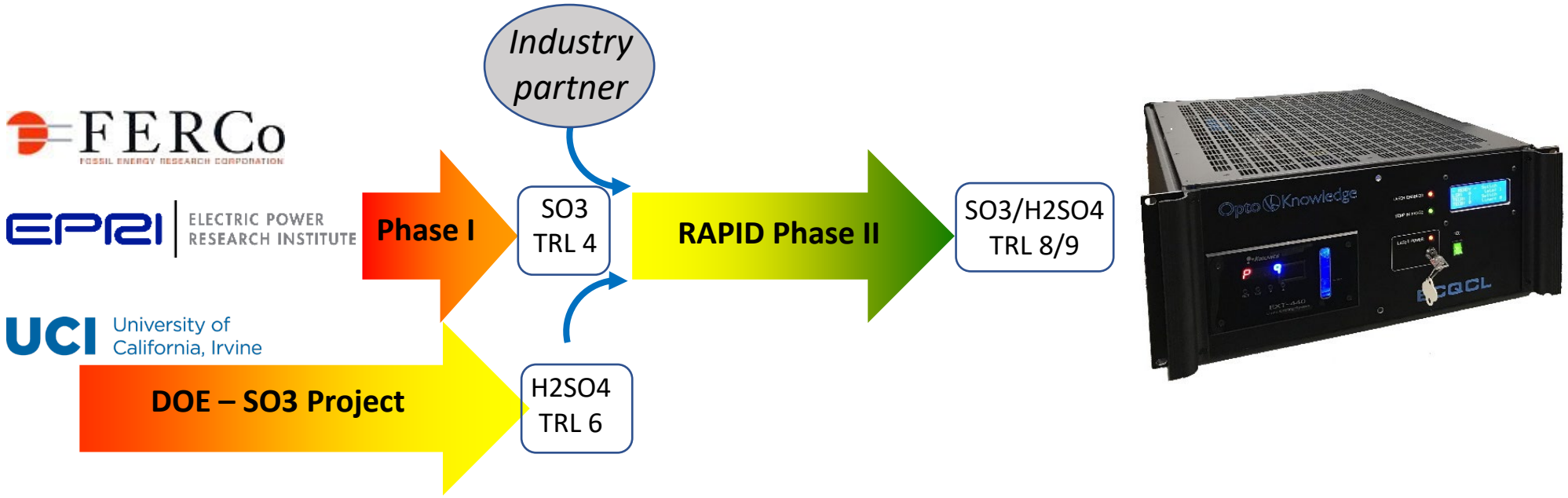
- Just wrapped up 3rd-year of project
- Two rounds of prototype development and testing to increase the Technology Readiness Level (TRL)
- Testing in laboratory (UC Irvine), industrial (FERCo), and Power Plant (Harrison Station) facilities

Project Status

- Successfully demonstrated ability to precisely measure H_2SO_4
- Successfully demonstrated at a coal-fired power plant
- Developed path for commercial SO_3 / H_2SO_4 sensor
- Industry feedback: “We need a solution now”



Related DOE/NETL SBIR



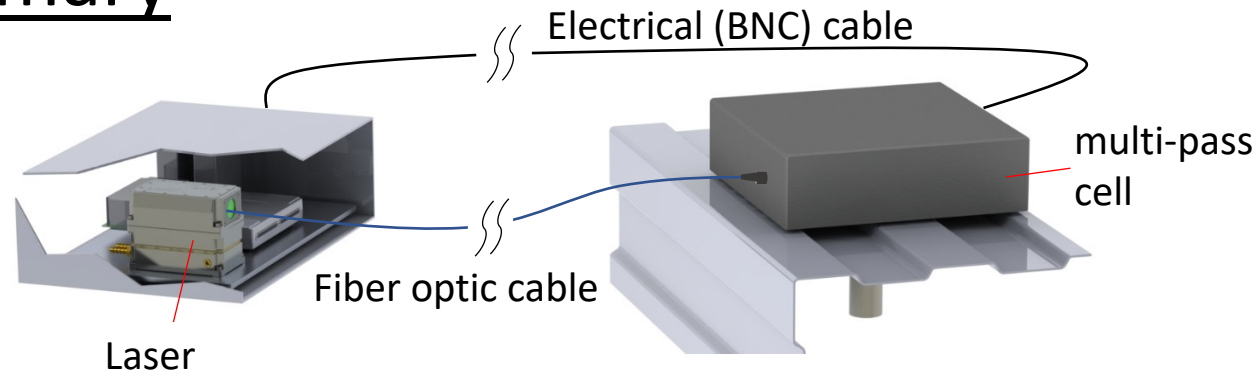
Related SBIR Project: Real-time Analysis with Pseudo In-situ Detection (RAPID)

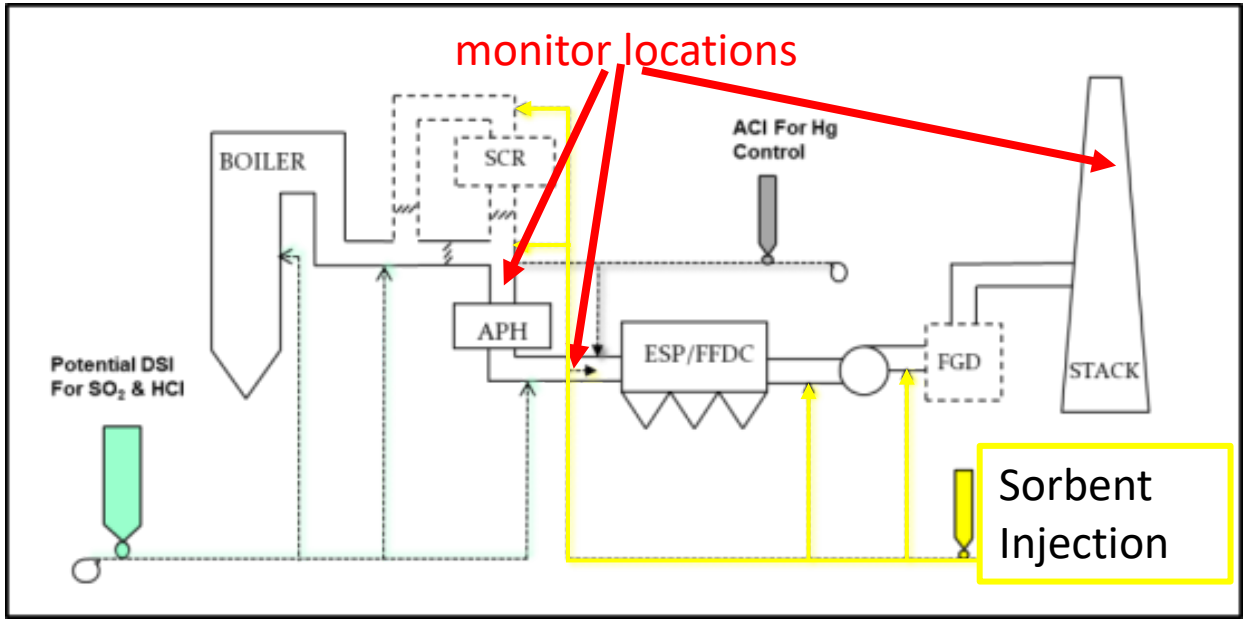
04:00 PM	Real-time, Close-coupled, Multi-species Gas Analyzer (SC0020879) Jason Kriesel, Opto-Knowledge Systems, Inc.

Summary

- A continuous SO_3 / H_2SO_4 monitor is needed to optimize sorbent injection
- Mid-IR Laser spectroscopy solution
- Advancing the state of the art
  - Broad tuning Mid-IR lasers
  - Hollow core fiber optics
  - Close-coupled, heated multi-pass cell
- Technology proven with 1 ppm sensitivity of H_2SO_4 at 1 Hz at a power plant
- Working on dual laser: SO_3 and H_2SO_4 system

Contact: jason.kriesel@optoknowledge.com





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