SO3/H2SO4 continuous real-time sensor demonstration at a power plant

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Abstract:

We present results from field testing of a new, innovative sensor developed to measure SO3/H2SO4 continuously and in real time at a coal-fired power plant. The system utilizes the sensitivity, specificity, and real-time capabilities of mid-infrared (Mid-IR) laser-based sensor technology, along with a heated, close-coupled cell mounted directly to a power plant duct. Measurements were made by the laser sensor over a 2-day period and compared to results from the accepted method, EPA 8A, which requires a 30-minute collection, labor intensive processing, and off-site analysis at a lab. In contrast to the condensation method, the laser sensor continuously samples flue gas and reports measurements of the concentration of SO3/H2SO4, SO2 ever second with unattended operation. This initial demonstration proved the sensor concept and paves the way for its use for optimizing sorbent injection used to neutralize SO3/H2SO4. Optimized sorbent injection will enable significant cost savings associated with efforts to mitigate the presence and effects of SO3/H2SO4 such as "Blue Plume", air heater fouling, and duct corrosion. In particular, the real-time, actionable information will enable better control of additive injection in flex conditions and variable fuels.

1 Introduction/Motivation

The need for an SO_3/ H_2SO_4 sensor is driven by two main factors: (1) environmental regulations on H_2SO_4 stack emissions with power plants and industrial facilities facing fines and other restrictions from a "blue plume" resulting from H_2SO_4 emissions and (2) damage and down-time due to the presence of SO_3/H_2SO_4, e.g., Ammonium Bisulfate (ABS) can form fouling the air heater. To neutralize SO_3/H_2SO_4, facilities inject a sorbent; however, without a monitor they are relying on historical records and are somewhat guessing as to how much sorbent to inject. This can lead to significant waste with over injection, or alternatively non-compliance for under injection. Facilities need a real-time continuous monitor of SO_3/H_2SO_4 for sorbent injection, similar to an ammonia slip monitor to optimize an SCR.

The current method for measuring SO_3/H_2SO_4 is EPA Method 8A[1] also referred to as "Controlled Condensation"; however, this approach is not appropriate for sorbent optimization. The method is labor intensive and disruptive. There is a significant amount of equipment that needs to be transported to the power plant, hauled up to the measurement location and then setup. The method then requires the insertion of a probe into a duct for a given period of time (~ 30 minutes) and then manually removed. A sample is collected through a labor-intensive process requiring another 30 minutes and the process repeated. Collected samples are sent to a lab after the campaign is finished with the results available typically days to even weeks later. The results are only a snapshot at one moment in time and cannot capture transients due to changing loads or fuels.

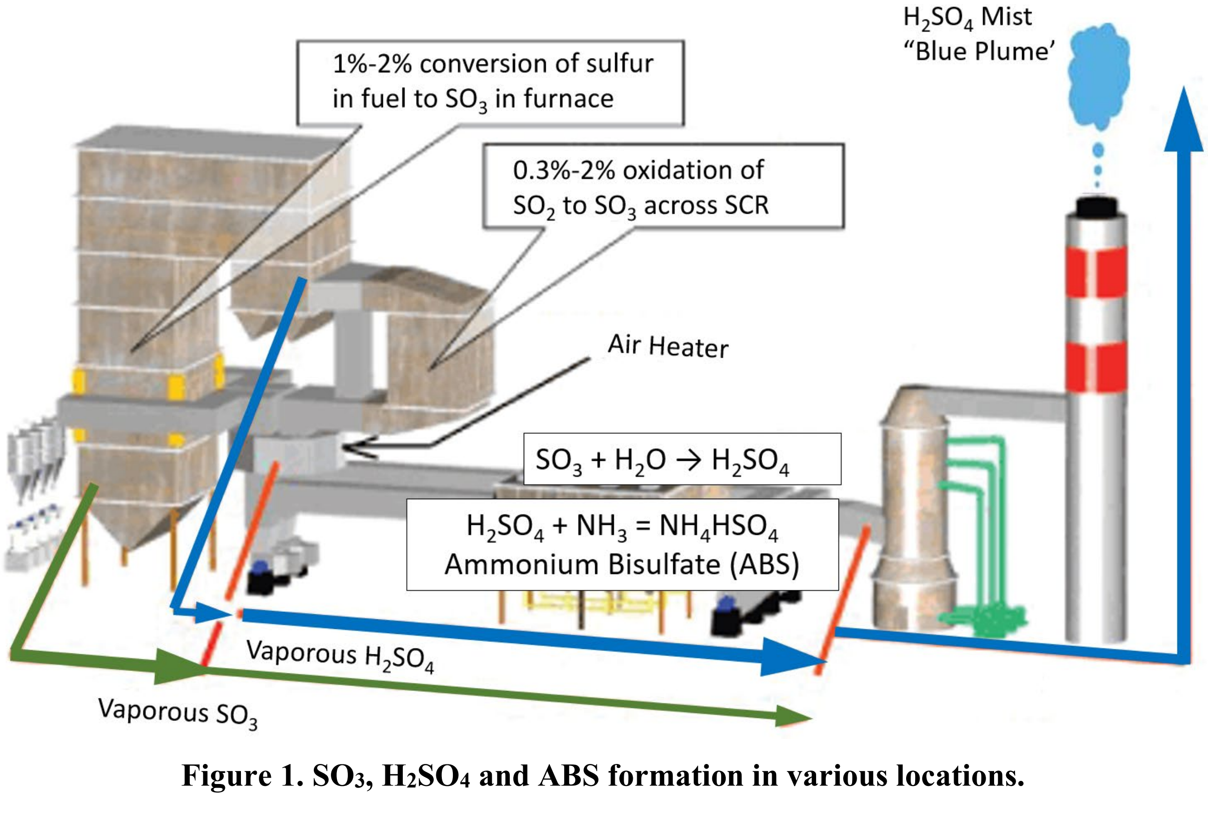
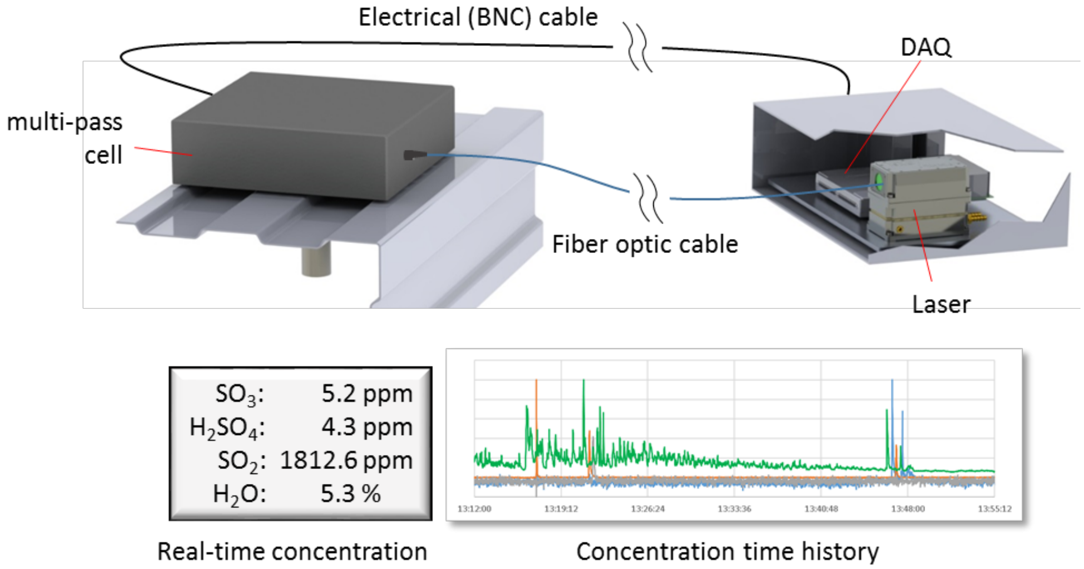


Figure 1. SO_3, H_2SO_4 and ABS formation in various locations.

2 Sensor System



Real-time concentration

Concentration time history

Figure 2. Simple diagram illustrating overall concept of sensor developed.

The primary objective of the work described here was to produce and demonstrate a continuous SO_3 / H_2SO_4 monitor for coal-fired power plants, a simple diagram illustrating the concept is shown in Figure 2. The monitor provides real-time, actionable information, which can enable control of additive injection. The system utilizes the sensitivity, specificity, and real-time capabilities of mid-infrared (Mid-IR) laser-based sensor technology, along with a close-coupled cell mounted directly to the ducting of a coal-fired power plant.

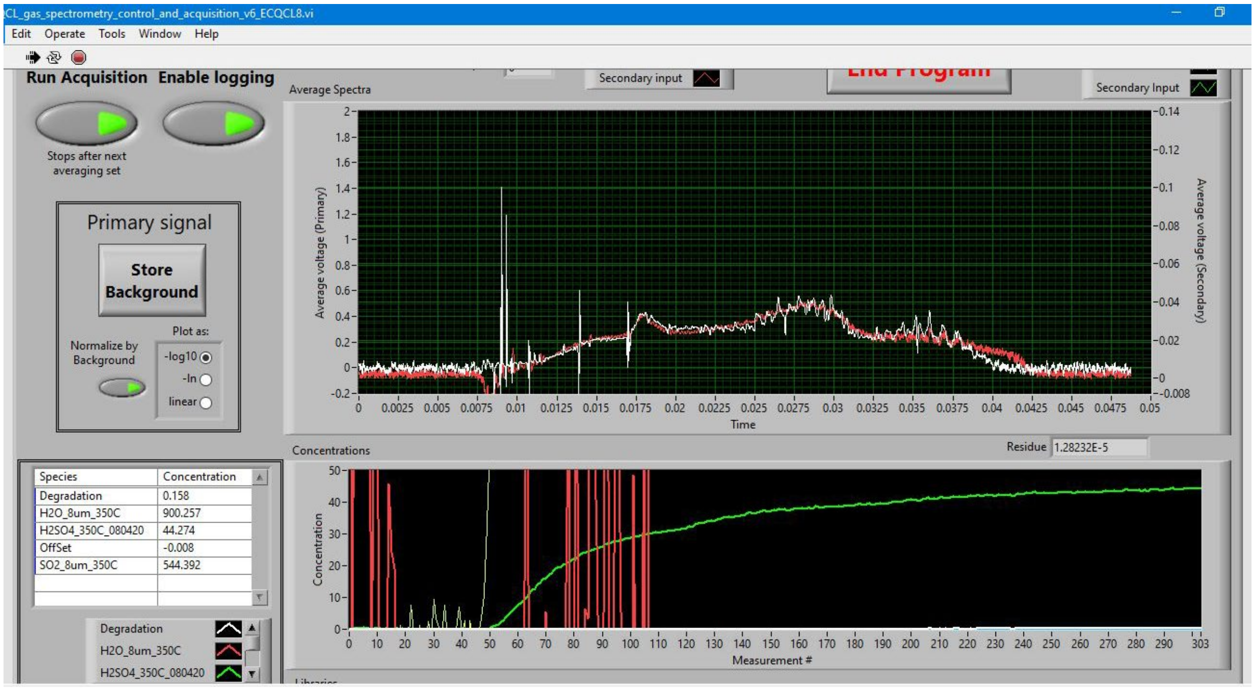
The developed sensors utilize tunable laser absorption spectroscopy (TLAS) operating in the mid-infrared (Mid-IR) wavelength region, which is the so-called “molecular fingerprint” region. Systems operating in the Mid-IR have orders of magnitude more sensitivity than systems operating at shorter wavelengths, such as near-infrared (NIR). However, NIR systems are more widespread due to more mature supporting technology (e.g., fiber optics, optical components, etc.).

We developed proprietary broad tuning lasers enabling the ability to effectively measure SO_3, H_2SO_4, H_2O, and SO_2. Different molecular species have unique spectral signatures that can be probed with lasers operating at different wavelengths. Standard TLAS uses relatively narrow wavelength tuning distributed feedback (DFB) lasers, which can typically only target a single species with narrow features, and are not appropriate for species with broad features, such as SO_3 or H_2SO_4. In contrast, by developing unique, broad-tuning laser technology, we were able to measure these species, as well as SO_2 and H_2O simultaneously. Furthermore, to enable real-time analysis at a power plant, we modified a commercially available heated gas cell to operate in the Mid-IR wavelength range and fiber coupled the lasers to enable remote delivery of the beams.

Since SO_3 and H_2SO_4 exist in a flue gas in a state of equilibrium, which depends on temperature and humidity, by measuring water concentration and controlling the temperature of the gas cell, we developed an approach to determine the total SO3 + H_2SO_4 concentration from just the H_2SO_4 measurement.

A commercial heated multi-pass gas cell was modified for the Mid-IR wavelength range by replacing windows and fiber collimator optics as well as the detector and detector optics. The two proprietary ECQCL systems were aligned through a 2.5 m long hollow fiber that was fabricated for transmission of Mid-IR lasers and produced by Guiding Photonics[2].

In addition to the hardware development, we developed a complete software suite which consists of ECQCL Data Acquisition software (Figure 3). The ECQCL Data Acquisition code performs laser tuning and data acquisition as well as real time spectral library fitting and concentration plotting simultaneously for all measured species.



Residue 1.28232E-5

Species	Concentration
Degradation	0.158
H2O_8um_350C	900.257
H2SO4_350C_080420	44.274
OffSet	-0.008
SO2_8um_350C	544.392

Figure 3. ECQCL Data Acquisition Software.

3 Lab Testing

To generate reference data (library spectra), the University of California Irvine (UCI) developed a catalytic SO_3 generation facility The facility consists of a heated catalyst bed, which converts SO_2 to SO_3 at temperatures ranging from 200°C up to 425°C. The gas flow from the catalyst is directed into the heated multi-pass absorption cell for the laser absorption measurements. Heated bypass channels allow for introduction of an additional gas stream to the mixture including the calibrated amount of water vapor in a range from 3% to 12%. Exhaust of the absorption cell can be directed into the condensation coil in order to perform standard EPA Method 8A for the SO_3 concentration measurements.

OptoKnowledge's proprietary external cavity quantum cascade lasers (ECQCL) were installed at the UCI flue gas facility to perform SO_3, H_2SO_4, and water spectroscopic measurements (Figure 4). Tests were performed for different concentrations of the species at three different cell temperatures of 350ºC, 300ºC and 250ºC. The result of this experimental work was a set of libraries for the species at different temperatures, Figure 5 and Figure 6.

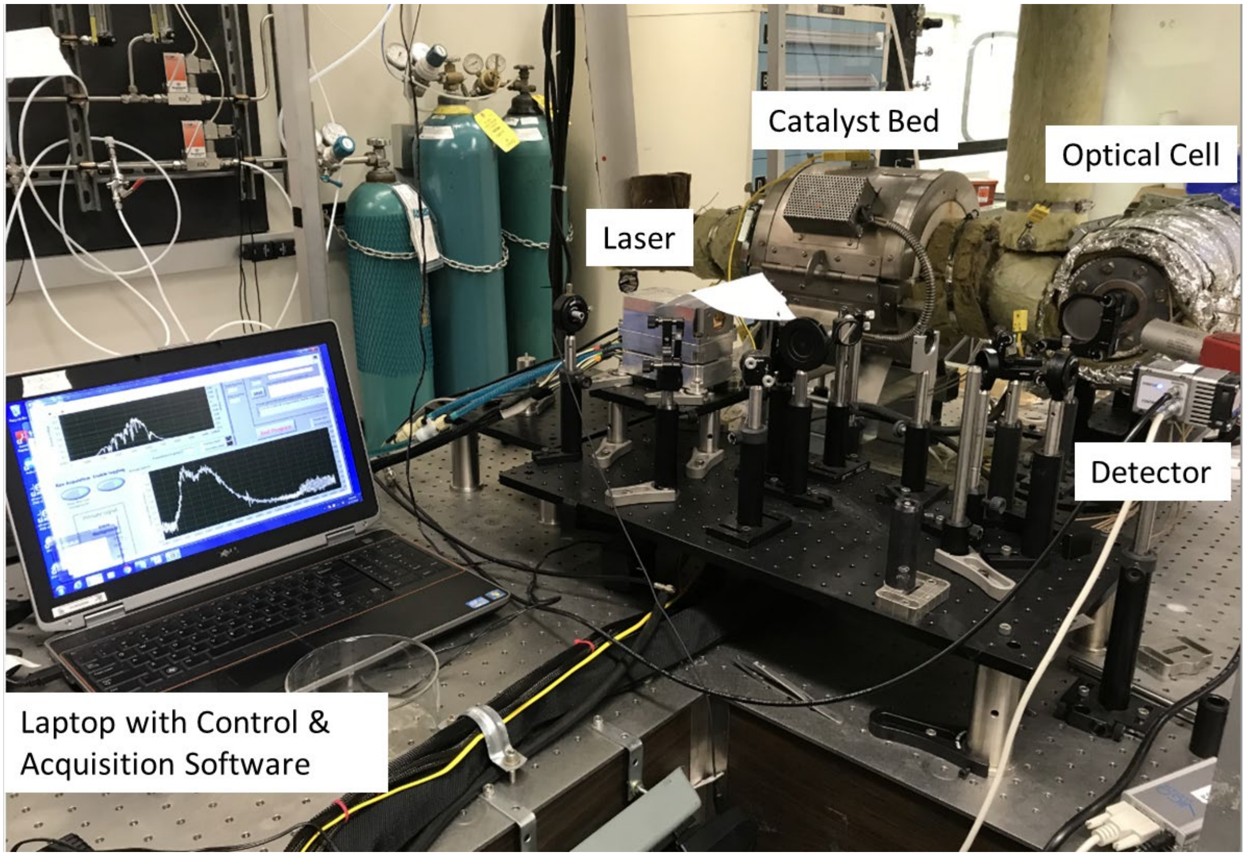


Figure 4. Measurement setup at UCI flue gas facility with ECQCL laser installed.

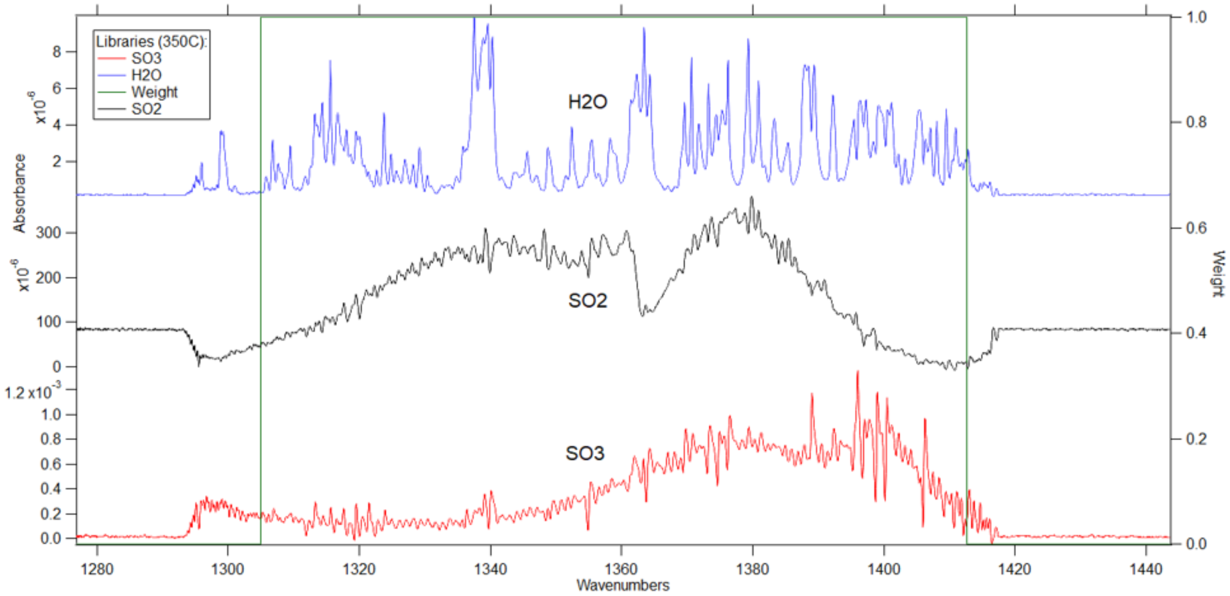


Figure 5. ECQCL7 libraries at 350°C. The "weight function" function is also shown, which in this case is a "top hat" function that essentially limits the wavelength range over which the data is fit.

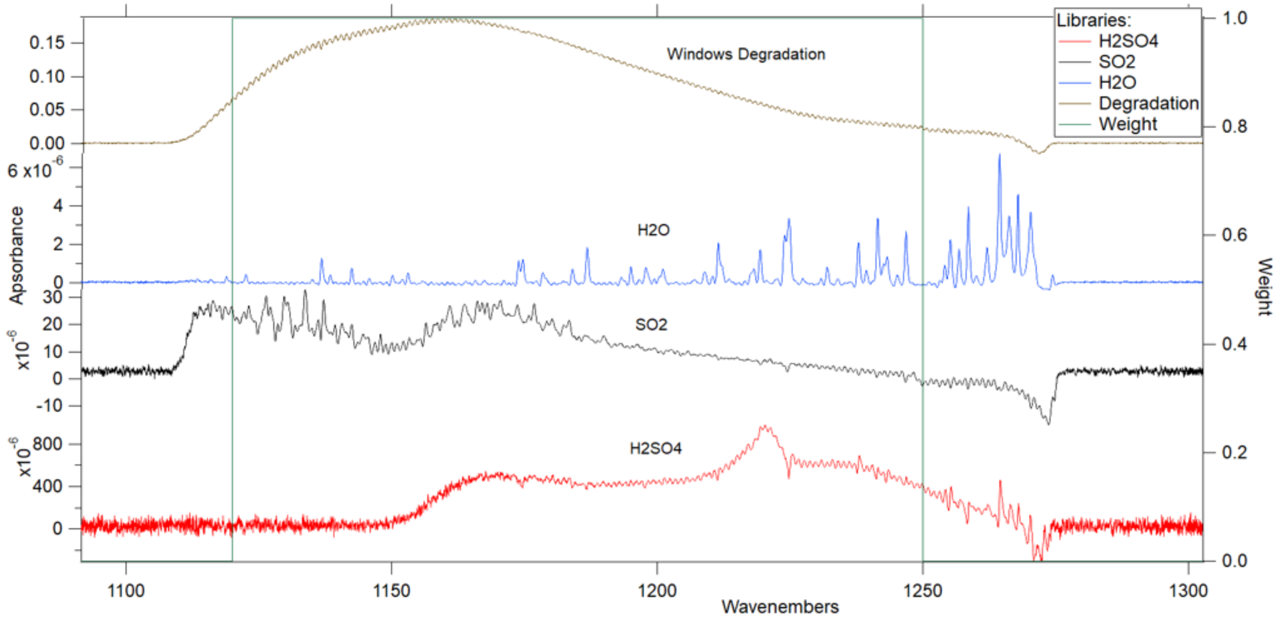


Figure 6. ECQCL8 libraries at 350°C, weight function and windows degradation function.

Testing campaigns were also conducted at the Fossil Energy Research Crop. (FERCo) which produces flue gas representative of a power plant using a natural gas combustor. By injecting SO_2 into the combustor region, FERCo can generate SO_3. The amount of SO_3 present in the flue gas is verified by controlled condensation (EPA Method 8A).

We demonstrated real-time 1 sec averaged H_2SO_4 measurements with the detection limit of 1ppm, (Figure 7). Measurements were performed as the temperature of the absorption cell was varied from 250ºC to 350ºC, which caused a change in the ratio between SO_3 and H_2SO_4 as measured by a corresponding change in H_2SO_4 (Figure 8). This shift is in agreement with equilibrium calculations based on the temperature of the cell and the water vapor concentration.

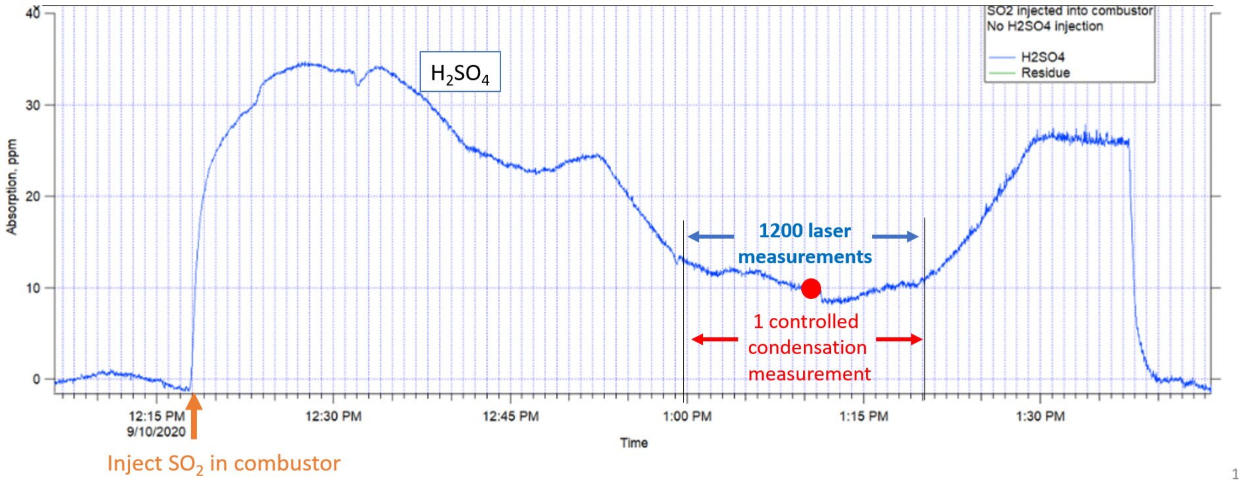


Figure 7. H_2SO_4 concentration measurements at FERCo. The gas cell temperature was varied, which resulted in changes in the concentration. Controlled condensation measurements verified the accuracy of the measurements; however, it takes 20 minutes to make one condensation measurement, during which we make 1200 laser measurements.

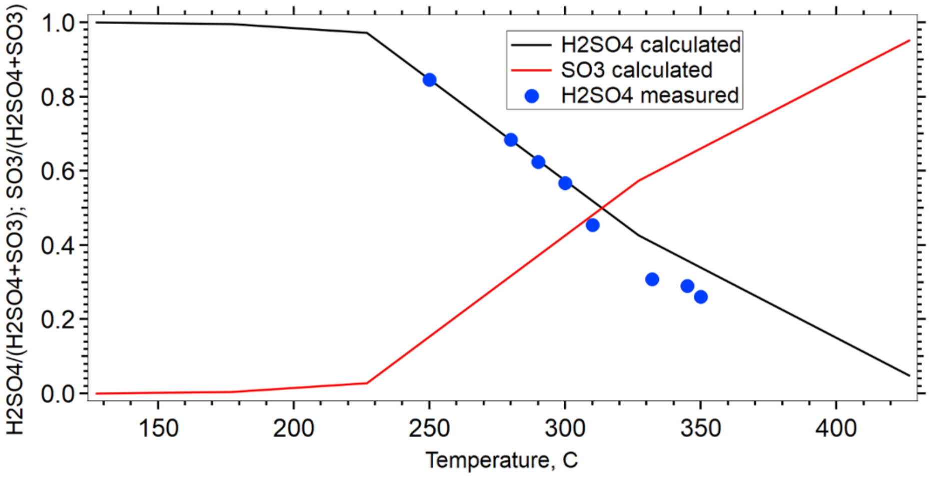


Figure 8. Shift in equilibrium ratio from H_2SO_4 to SO_3 with increase in cell temperature.

4 Field Testing

Field testing was conducted at a coal fired power plant. The system was set up on a duct port downstream of the SCR and upstream of the air preheater (Figure 9). Controlled condensation (EPA Method 8A) measurements were collected to validate the laser measurement. However, the condensation measurements require sample collection and then lab analysis of the sample and do not provide real-time measurement capability. In addition, the control method cannot distinguish between SO_3 and H_2SO_4, as a result, it produces a single measurement of concentration which is a sum of concentrations of both species. The laser monitor produces measurements of H_2SO_4 only and we calculate the total H_2SO_4+SO_3 by utilizing the equilibrium equation along with measurements of cell temperature and water vapor concentration.

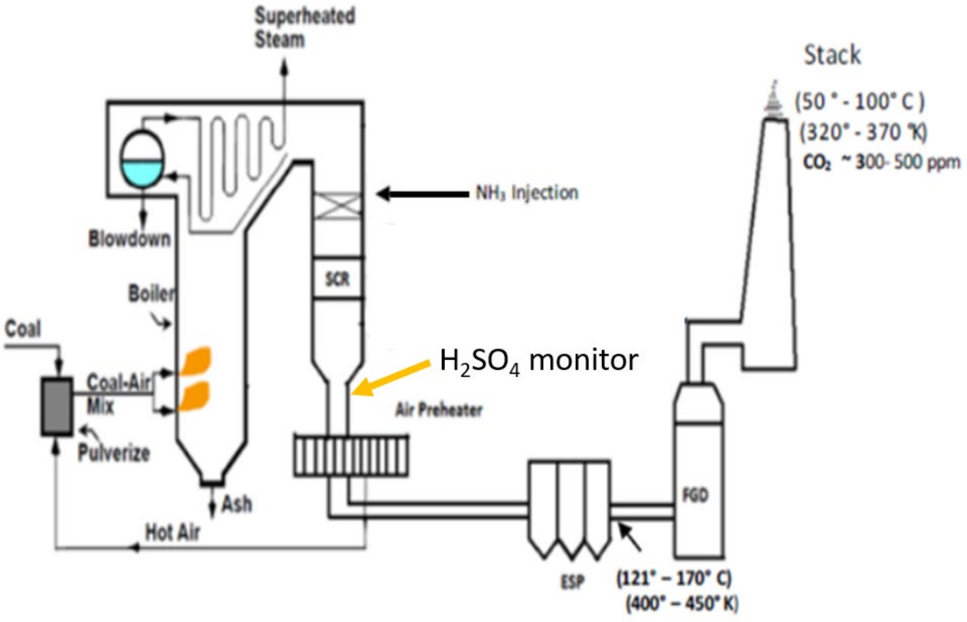


Figure 9. The H_2SO_4 monitor was installed between SCR and air preheater at the power plant (orange arrow).

The laser H_2SO_4 monitoring system consists of the gas cell, control box, ECQCL system and laptop (Figure 11). The gas cell was mounted on the duct port with the probe lowered inside the duct to collect the sample. The control electronics box was connected to 220VAC and instrument air. The ECQCL laser beam was delivered to the gas cell via a Mid-IR hollow-core fiber optic. A laptop computer was used to operate the system and collect data.

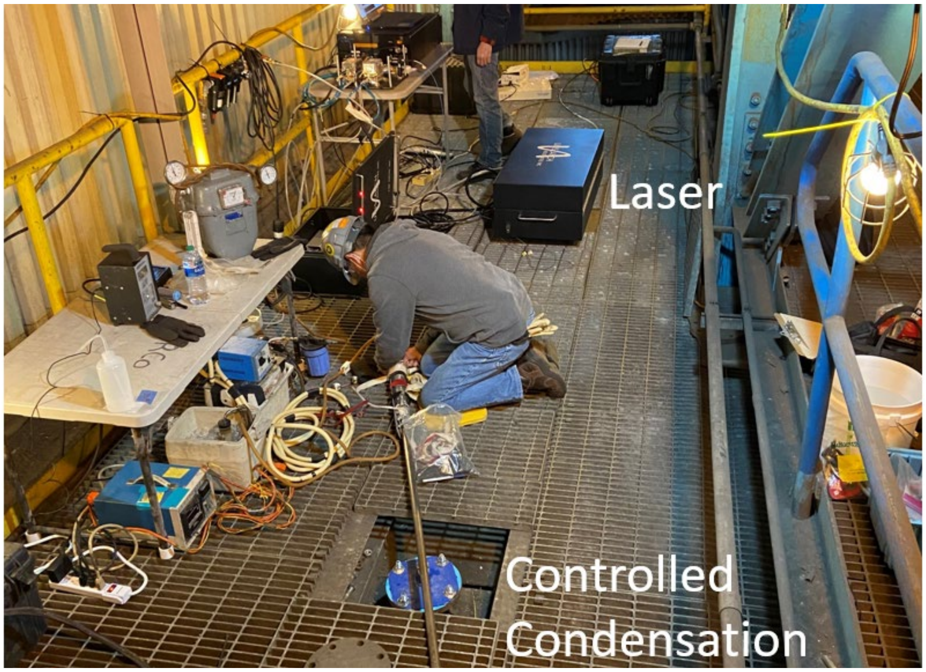


Figure 10. Controlled Condensation was performed on port next to the laser monitor.

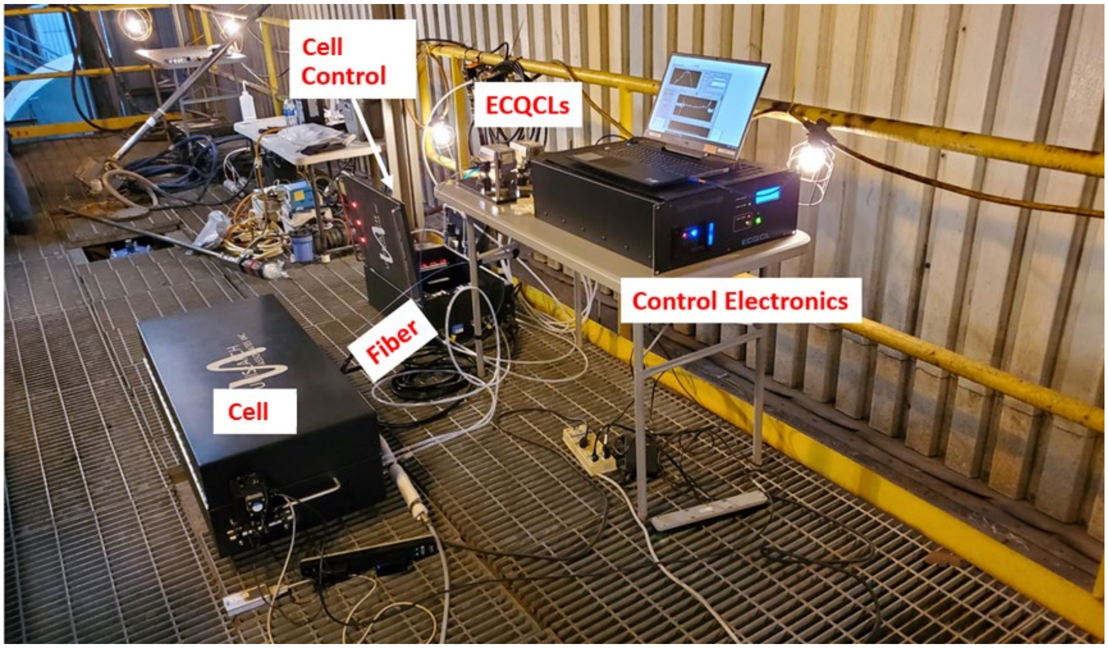


Figure 11. H_2SO_4 monitor installed with the sampling probe inserted into the duct.

Figure 12 displays a sample of two hours of data acquisition. The measurements are done in real-time with 1 second resolution for all the measured species: H_2SO_4, SO_2 and H_2O. As can be seen on Figure 12, during the measurements we periodically performed a nitrogen purge of the cell with the goal of acquiring a clean background. That procedure is effectively “zeroing” the instrument.

In general, the laser system measurements of H_2SO_4 were lower than measurements produced by controlled condensation. For example, in the data shown in Figure 12 for the time period from 12:30PM to 1:00PM, the laser system measured 28 ppm H_2SO_4 with a total SO_3 + H_2SO_4 concentration of 41 ppm. Under similar conditions, controlled condensation measured 54 ppm for the total SO_3 + H_2SO_4 value. We believe that the laser system produced lower readings due to losses in the sampling train. Variations on the sampling procedure were tested at the power plant and we have a design for an improved sampling method that should close the gap between the laser measurements and controlled condensation in future utilizations.

The power plant test was a successful demonstration of the technology. We demonstrated real-time, continuous monitoring of H_2SO_4, SO_2 and H_2O. The system worked reliably unattended on the duct port. Lessons learned from the tests are now being used to further improve the design.

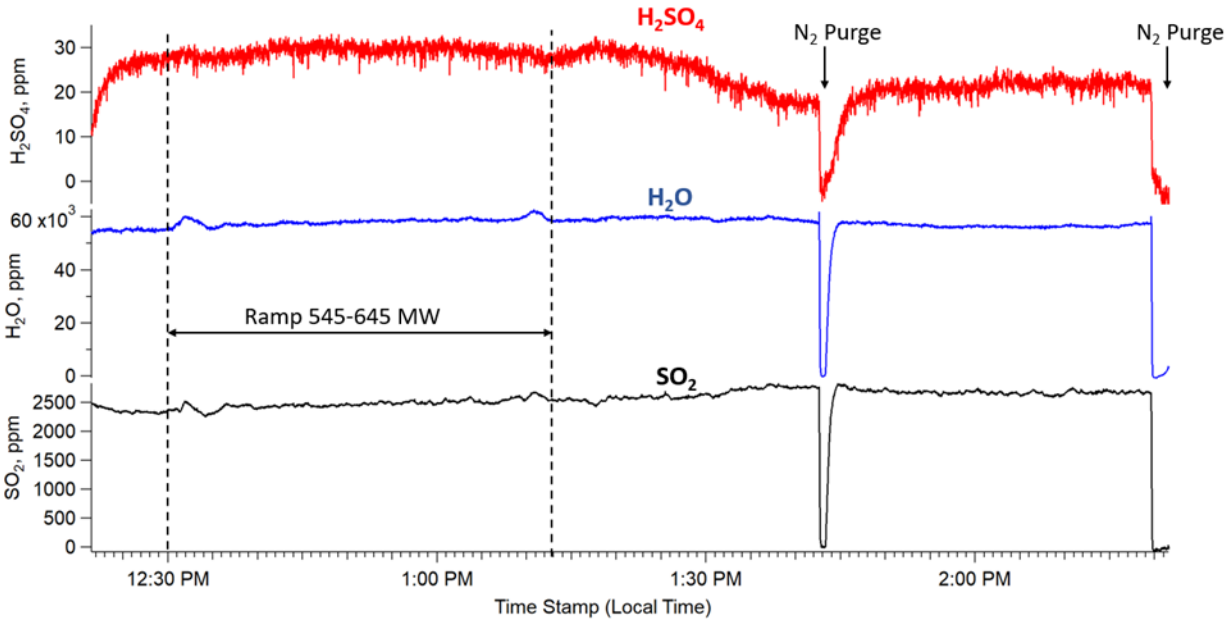


Figure 12. Example of measured data showing two hours of real-time H_2SO_4, SO_2 and H_2O measurements. N_2 purge is done to acquire the background spectra. At about 1:30PM the cell temperature was changed shifting the equilibrium toward SO_3.

5 Acknowledgements

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6 References

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[1] https://www.epa.gov/sites/production/files/2020-08/documents/ctm-013_0.pdf

[2] https://guidingphotonics.com/mid-infrared-mid-ir-fiber-optic-solutions/