Real Time Continuous Monitoring of SO_3 and SO_2 Across Flue Gas Ducts

Curtis Laush, Ph.D., IMACC
Round Rock, TX
claush@imacc-instruments.com

Greg Coleman and Brian Adair, Geosyntec Consultants
Charlotte, NC
GColeman@Geosyntec.com

Why SO_2 and SO_3 Monitoring?

- $SO_3 + H_2O \rightarrow H_2SO_4$ mist at the stack, i.e. "Blue Plume"
- SO_3 significantly reduces the efficiency of activated carbon for mercury capture
- SO_3/H_2SO_4 corrodes equipment
- $SO_3 + NH_3$ forms ABS, which clogs catalysts, air heaters and other equipment
- SO_2 oxidation changes over time in the SCR, which can actually <u>increase</u> SO_3
- <u>Continuous</u> measurement of SO_2/SO_3 allows for the optimization of sorbent injection toward its removal

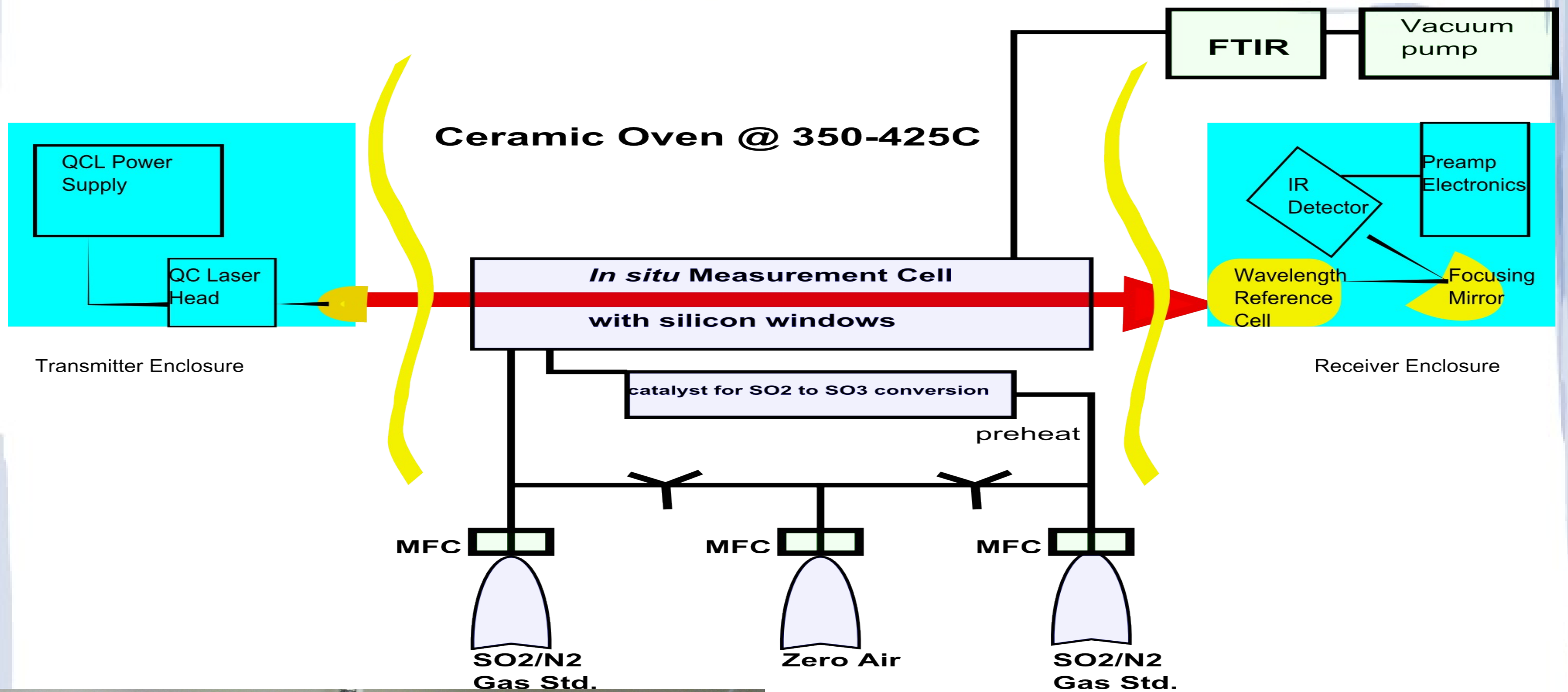
Remote Sensing of SO_3 by Quantum Cascade Laser (QCL)

- A distributed feedback (for single mode/frequency output) QCL is mounted in air purged, temperature controlled, weather proof (NEMA) housings with a dual lens refracting telescope to collimate the infrared beam.
  - Data acquisition system can be located hundreds of meters away
  - System can be remotely controlled by cellular modem

- Center frequency of laser output selected to maximize SO_3 sensitivity while minimizing SO_2 and H_2O interferences (but still allowing for quantification of SO_2 and H_2O along with SO_3). Scanning range ~4 cm^{-1}.

Monitoring of SO_2/SO_3 by QCL: Calibrations

- The generation of calibrated spectroscopic references is very challenging, given the sensitive nature of the $H_2SO_4 \leftrightarrow SO_3 + H_2O$ equilibrium.
- SO_3 generated in a heated (350-425 ^oC) cell by passing pre-heated dry SO_2/air mixtures over a catalyst at moderate flow rates.
- SO_2 to SO_3 conversion is tracked through real-time monitoring of SO_2 concentrations by extractive FTIR. Conversion efficiencies consistently maintained at ~95%.
- QCL spectra of SO_2 and SO_3 are recorded as quantitative references; $SO_2/SO_3/H_2O$ mixtures were also generated for evaluation purposes.



The SO_3 generation and certification scheme will be miniaturized and utilized as a field validation system.

IMACC

Cross Duct Field Monitoring of SO_2/SO_3

- *In situ* (cross duct) monitoring eliminates extraction issues (tubing contamination, sample losses, chemical equilibria shifts, etc.) making $SO_3/SO_2/H_2O$ measurements representative.
- Objective: Measure multiple compounds simultaneously and in real time with high resolution in time (< 1 minute) and concentration (< 1 ppm). Detection limits on the order 2.5 ppm*m (500 ppb in 5m duct).
  - SO_2, SO_3, NH_3, H_2O, NO, NO_2, N_2O, CO, CO_2, …
- Integrate gas concentrations over the laser path to quickly get whole duct average concentrations.
- The first field study was conducted with an open-path QCL monitoring system operating as a *bistatic* CEM. Beam path located directly downstream of an SCR outlet. Flue gas temps ~700 F, lime injection was being employed.

Cross Duct Monitoring of SO_2/SO_3 (cont.)

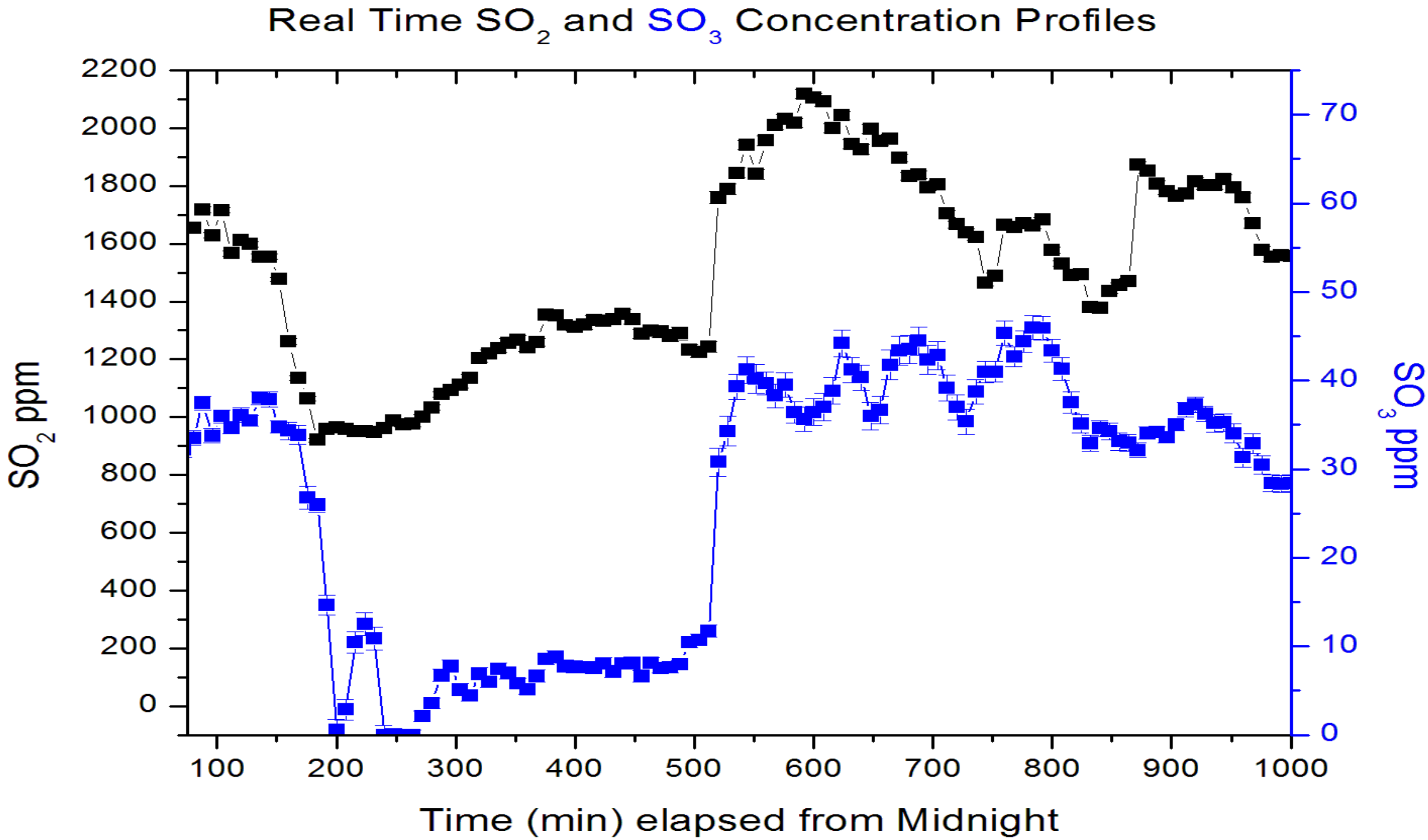
Transmitter

Receiver

Angle iron

IMACC

Example of Monitoring Data



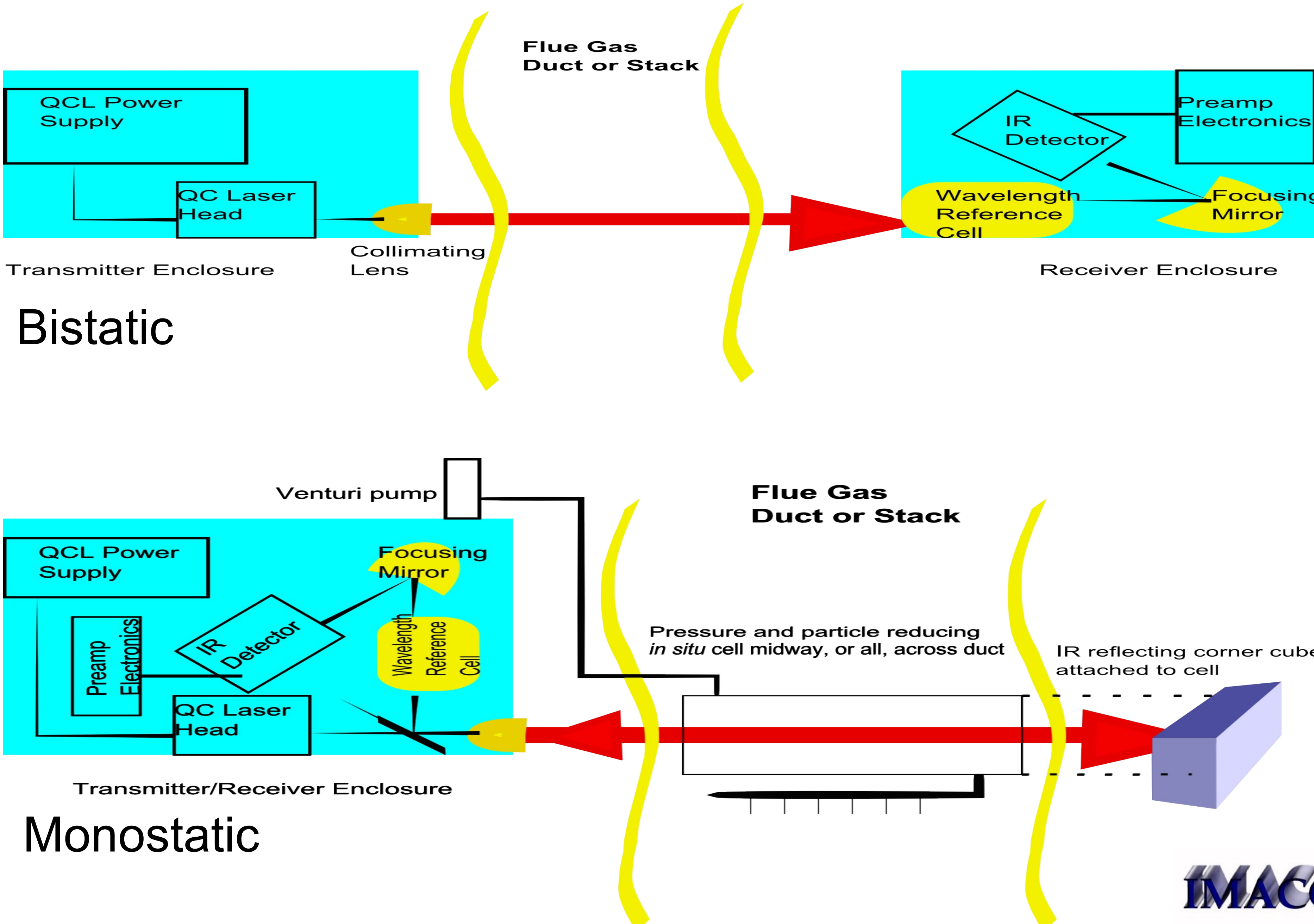
Field Test Conclusions

- QCL monitor ran continuously for a designated three week period after installation while maintaining alignment.
- *The real-time SO_2 concentrations from the QCL system were found to agree favorably with in line “reference” CEM measurements.*
- *The averaged real-time SO_3 concentrations from the QCL system were found to be comparable with concurrent CCS measurements.*
- A small degree of measurement variability and higher detection limits have been introduced into the real-time SO_3 results due to low resolution SO_2/SO_3 spectral overlap at ambient pressures and laser power fluctuations.
  - Which becomes apparent, for these molecules, at gas pressures exceeding ~0.4 atm.
  - A design modification has been implemented to mitigate these effects:

Geosyntec.com
engineers | scientists | innovators

IMACC

Possible Sampling Configurations for the QCL System



Monostatic (with *In Situ* Cell) vs. **Bistatic** QCL System

- Reduced pressure sampling region for best spectral resolution, leading to lowest measurement variability and SO_3 detection limits (~2.5 ppm*m).
- Requires less infrastructure and resources; only one sampling port, and compressed air and power for one enclosure is needed.
- Better spectral resolution and reduced pressures enable quantification of H_2O, in addition to SO_2 and SO_3.
- Slightly more cost, but now a truly portable field monitoring system without alignment issues.

- Measurements for SO_2 and SO_3 conducted under native pressure conditions (SO_3 DL ~ 5 ppm*m).
- More measurement variability is introduced.
- Resources required for two devices; coaxial sampling ports needed.
- Less complexity and cost.

IMACC

Conclusions

- The QCL monitor is a viable CEM system, or it can be used as a field sampling project monitoring tool.
- Bistatic QCL system available now, monostatic QCL system to be field demonstrated by May 2012 (probe now undergoing lab testing).
- It can be implemented at the inlet/outlet of the SCR, air heater, or stack (SO_2/SO_3/H_2O calibrations are available at temperatures ranging from ~100 – 425 C).
- Applications include:
  - Track real time changes in SO_2 oxidation across catalyst and downstream
  - Track potential SO_3 dew points when optimizing air heater operation
  - Optimize sorbent usage for SO_3 mitigation