Detection of Sulfur Dioxide by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)

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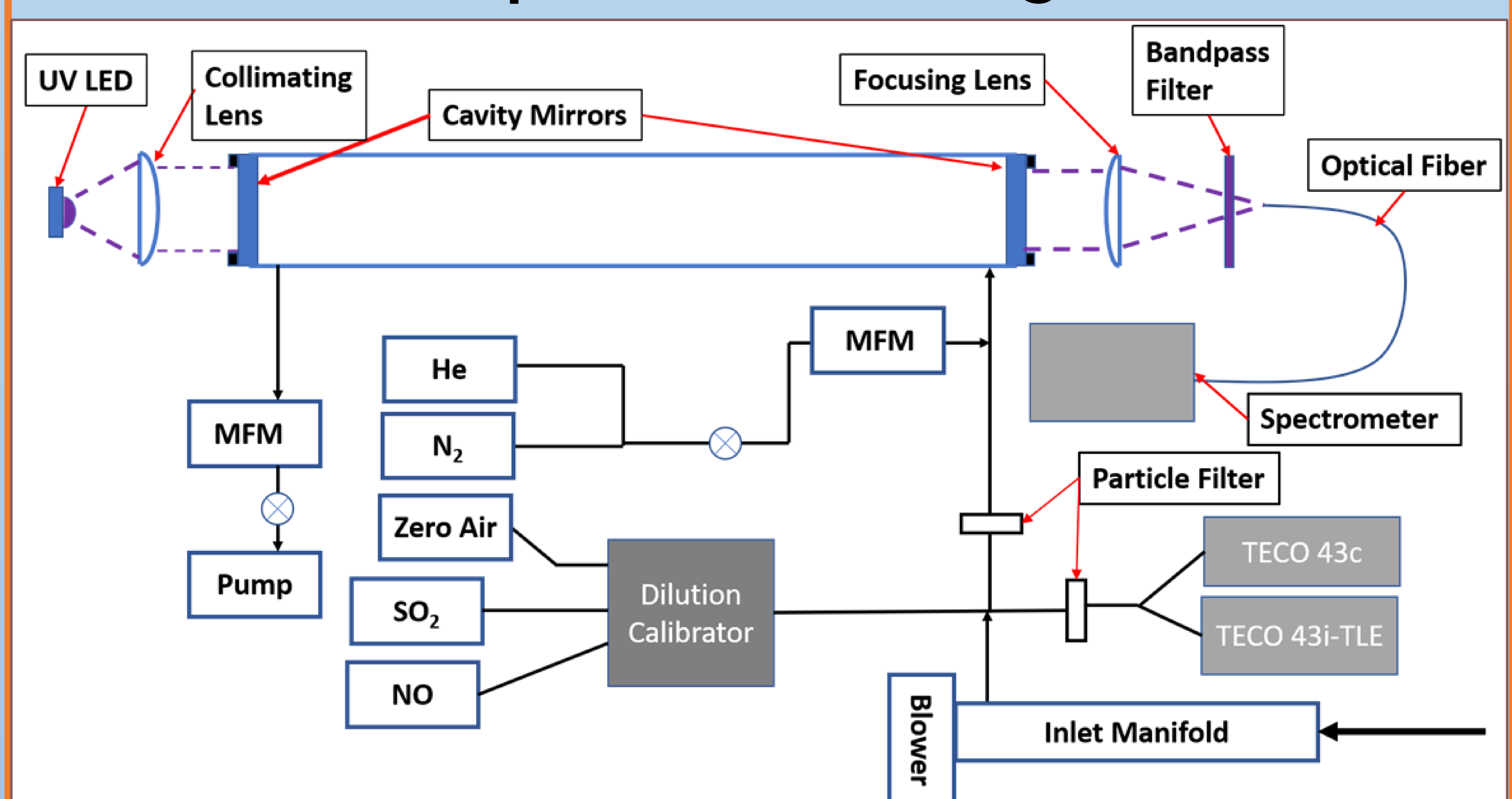
Background

- Sulfur dioxide (SO_2) is an important precursor for formation of atmospheric sulfate aerosol and acid rain
- Emitted anthropogenically through the combustion of coal and oil
- Emitted naturally from volcanic eruption or atmospheric oxidation of sulphur species
- SO_2 has direct health effects
    - Respiratory problems
- Proven to have a short-term cooling effect on global climate
    - Geoengineering
- Despite regulations SO_2 emissions in the US and Europe are still rising
- Variety of techniques for SO_2 measurement; UV fluorescence most common
- Uses pulsed UV light to excite SO_2 molecules which relax and emit light at a longer wavelength
    - Known to have interference from NO, H_2O, m-xylene, acetone
    - Most instruments include a hydrocarbon scrubber
    - Detection limit of 0.208 ppbv for a 10 sec average
    - Detection limit of 0.05 ppbv for a 300 sec average with 1% or 0.2 ppbv precision

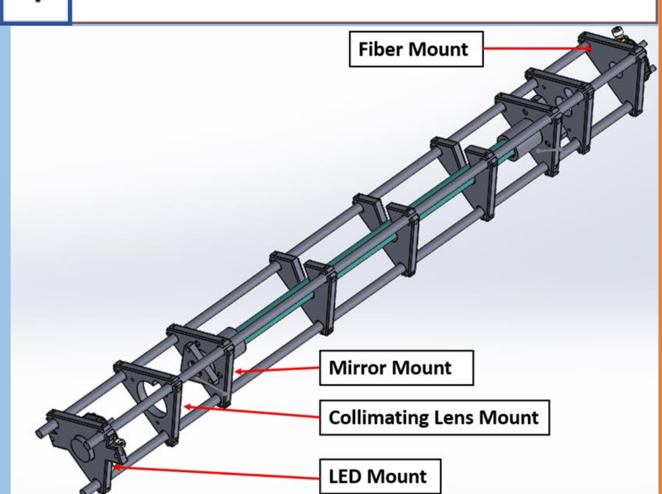
Aims of Research Project

- Use Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS) to produce an instrument that will:
    - Have similar, if not lower, detection limits than commercially available instruments
    - Be portable
    - Not suffer from interfering molecules
    - Cheaper

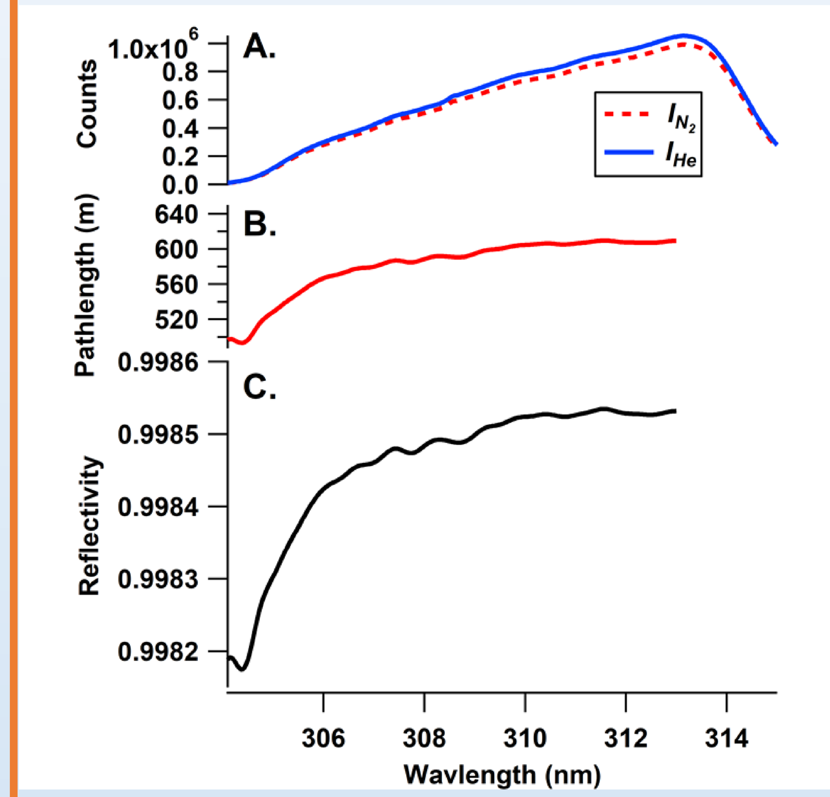
Experimental Design

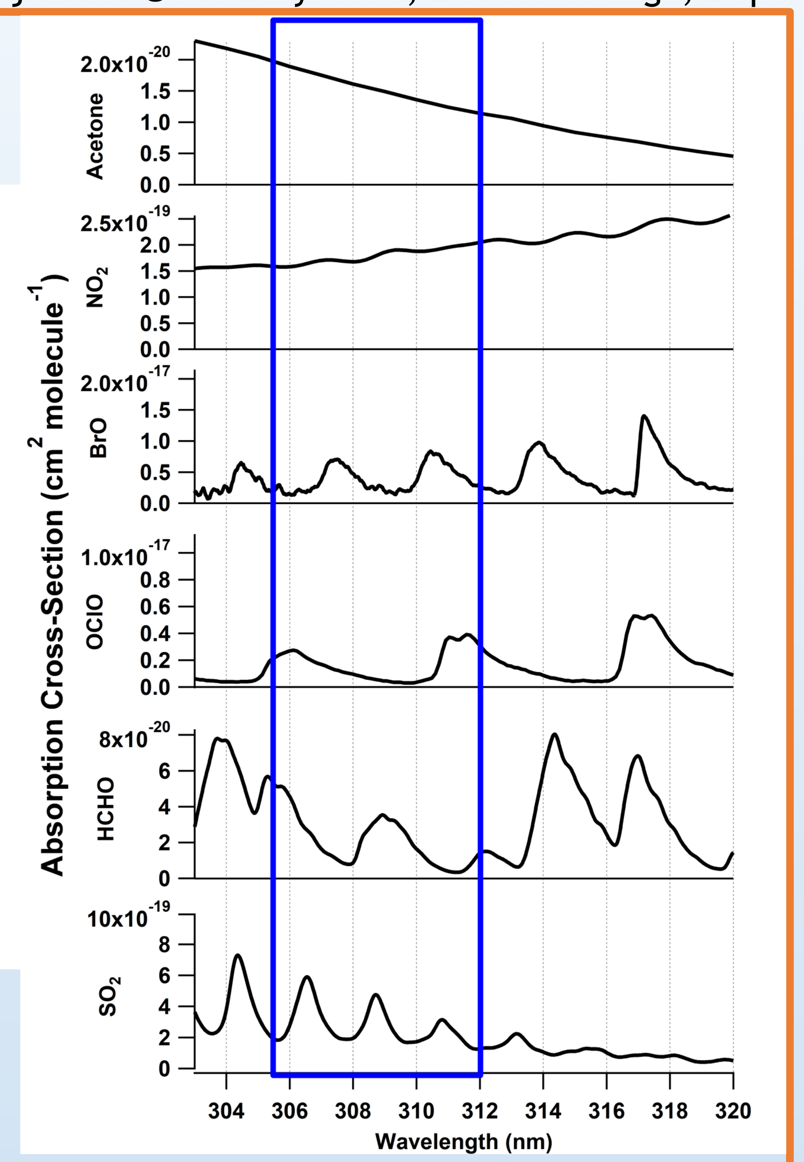


Above: Schematic of BBCEAS cavity as set-up for comparison with the SO_2 standard and ambient sampling. Flow is pulled into the system, and the total flow of the sample and the overflow are measured by mass flow meters (MFM). BBCEAS measurements are made in parallel with the Thermo Electron Corporation (TECO) 43 series instruments.



Right: CAD image of the 3D printed cavity





Left: Shows how the path length and reflectivity is calculated by using He and N_2 gasses as reference gasses for calibration. Changes in these values over wavelength is also shown
Right: An example of spectra for species that absorb in the same region as SO_2

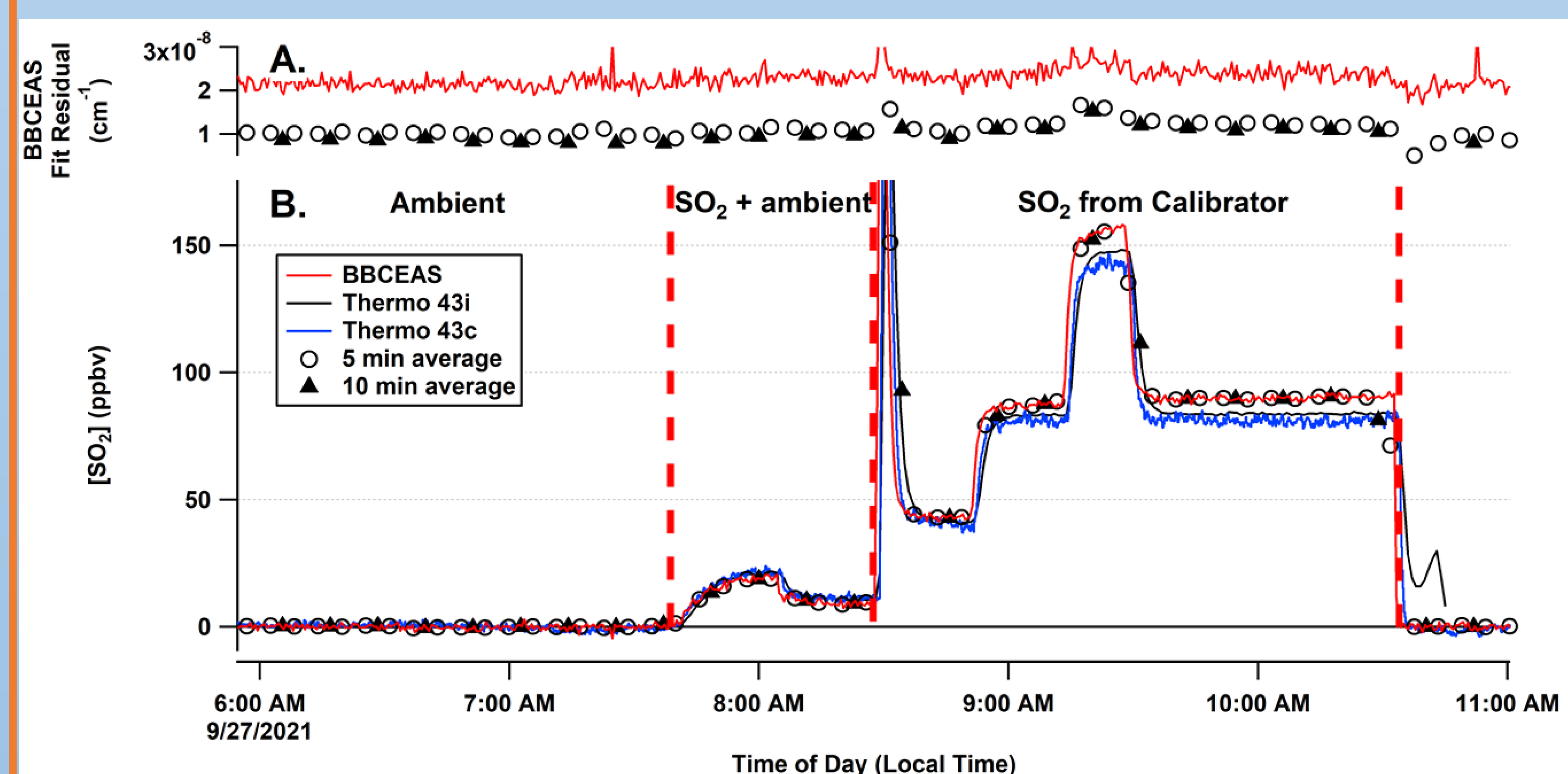
- Gas is pulled into the cavity
- Light is bounced between the highly reflective mirrors (R=0.9985) for an effective path length of ~575 m
- Reflectivity is calculated using N_2 and He as reference gasses with known Rayleigh scattering
- The measured SO_2 absorbance spectrum is fit using known absorption cross-sections and a concentration calculated as follows:

1. $$R(\lambda) = 1 - d_0 \frac{\left(\frac{I_{N_2}(\lambda)}{I_{He}(\lambda)}\right)\epsilon_{Ray}^{N_2}(\lambda) - \epsilon_{Ray}^{He}(\lambda)}{1-\left(\frac{I_{N_2}(\lambda)}{I_{He}(\lambda)}\right)}$$

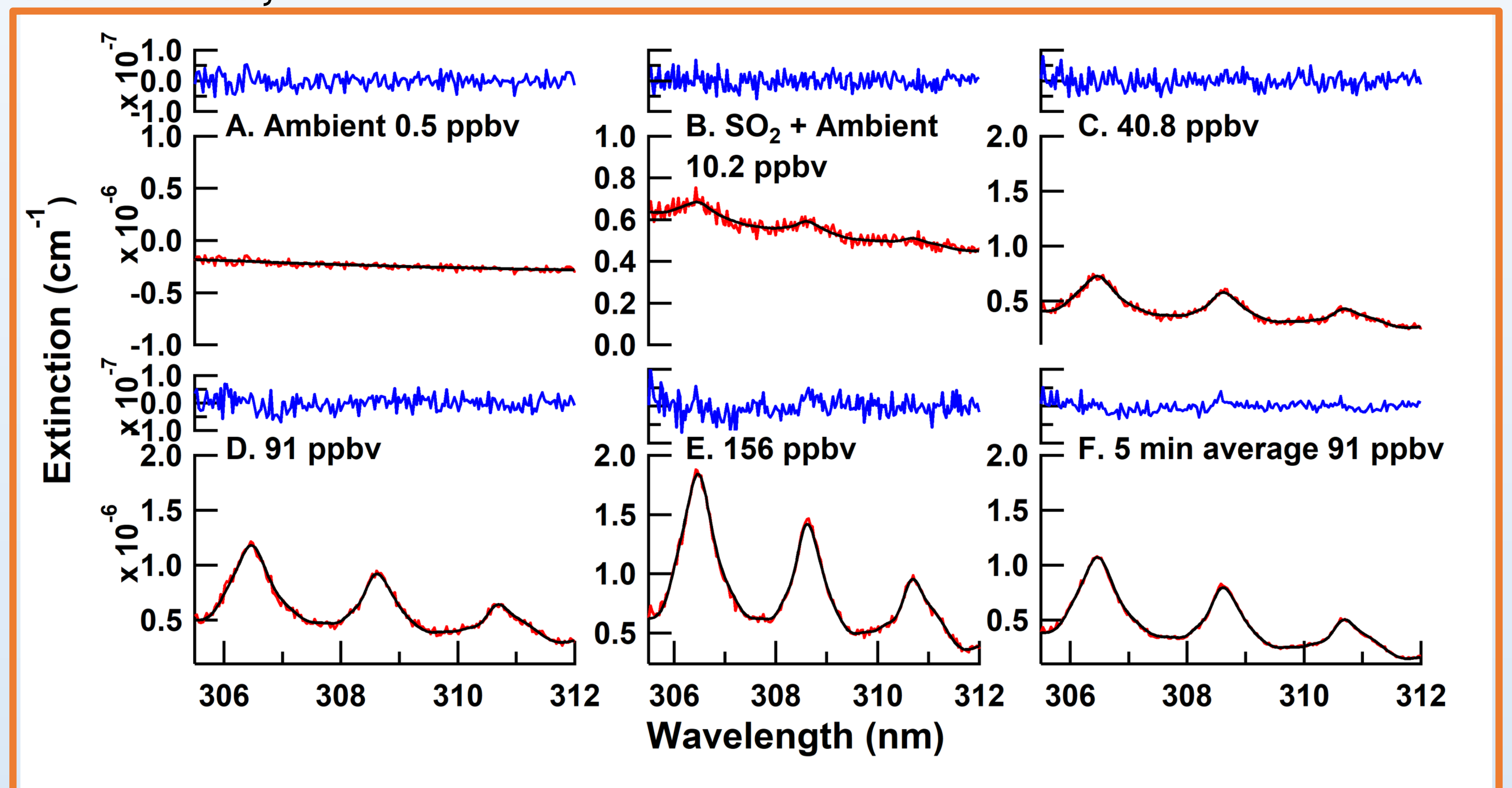
2. $$\epsilon(\lambda) = \left(\frac{1-R(\lambda)}{d_0} + \epsilon_{Rayleigh,Air}(\lambda)\right)\left(\frac{I_0(\lambda) - I(\lambda)}{I(\lambda)}\right)$$

3. $$\epsilon(\lambda) = \sigma_{SO_2}(\lambda)[SO_2] + \sigma_{NO_2}(\lambda)[NO_2] + polynomial$$

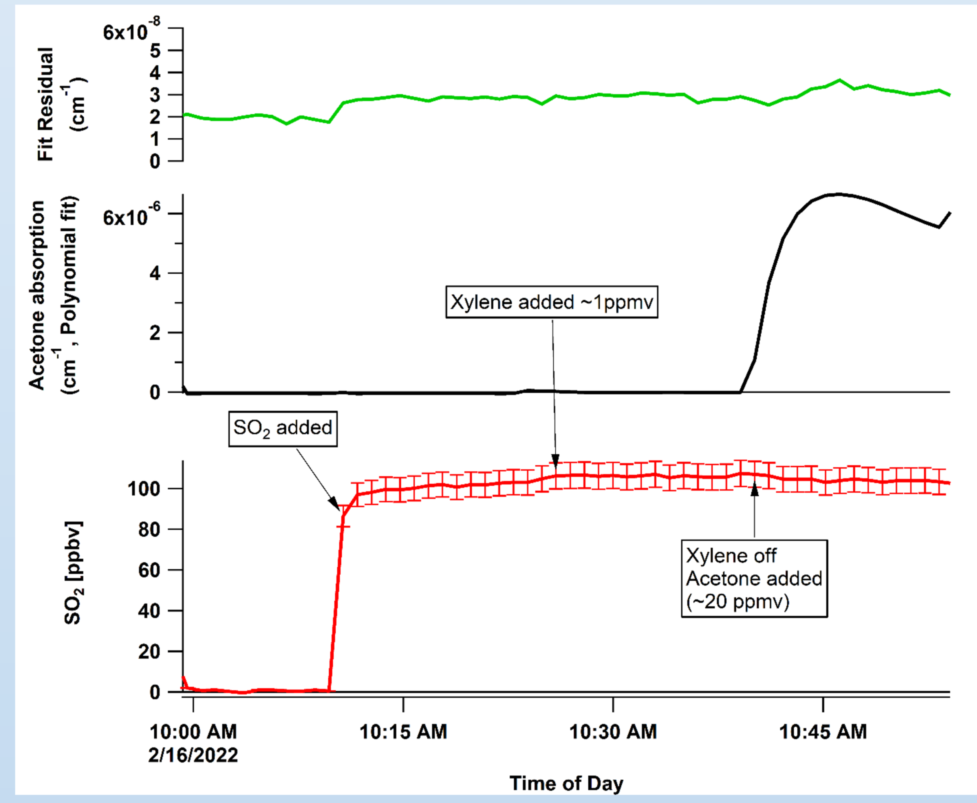
Results and Discussion



Time series of retrieved SO_2 concentrations. Panel A shows the 1-σ standard deviation of the fit residual for the 30 second, 5-minute and 10-minute data. Panel B shows the measured SO_2 from the three instruments under ambient, SO_2 + ambient, and calibration conditions as well as the time traces for the 5- and 10-minute averaged data. Vertical red dashed lines separate the different conditions. The jump in the 43i signal at the end of the experiment is due to a flow connection change to that instrument.

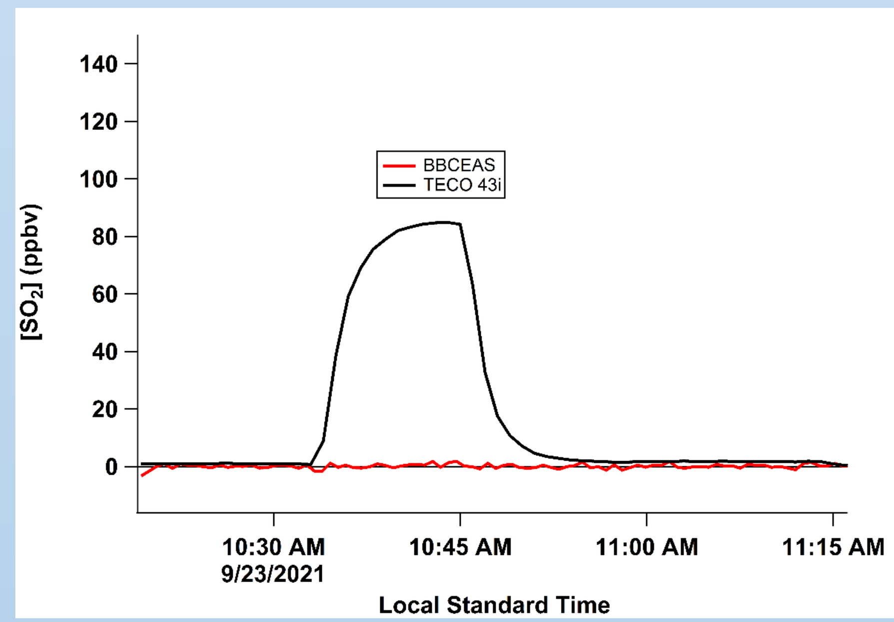


Comparison of SO_2 detection with different averaging and SO_2 concentrations



Left: Trial that shows that there is no interference in SO_2 detection from acetone or xylenes

Right: Difference between the Thermo TECO 43i and BBCEAS when NO (interferant) is present in the sample



Conclusions

- Overcomes interferences by other species
- Comparable limit of detection
- More portable
- Hourly level detection limits are similar
- BBCEAS detection limits: 2.6 ppbv 30 sec sampling
  0.75 ppbv 5 min averaging
- Other detection limits: 130 ppbv constant sampling
  3.6 ppbv averaging

Future Work

- Unmanned Aerial System (UAS)
    - Lower power requirements
    - Tropospheric testing for large emitters
- Improvement of detection limit
    - UV-range LED development
    - Improvement in S/N from spectrograph
- OH radical detection using BBCEAS

Thalman, Bharwaj, Flowerday, and Hansen; Detection of Sulfur Dioxide by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS), 2022, *submitted*.