A 3D-printed Broadband Cavity Enhanced Absorption Spectrometer (BBCEAS) for the measurement of Sulfur Dioxide

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Introduction:

Cavity enhanced spectroscopy techniques leverage highly reflective mirrors to allow for long extinction path lengths (100's of meters to >10 km) in a compact footprint(~1 m). A broad-band cavity enhanced absorption spectrometer was constructed to measure SO_2 in the wavelength range from 300 – 320 nm. SO_2 is a product of combustion from the oxidation of sulfur impurities at high temperatures. SO_2 is an EPA Criteria Pollutant and is linked to acid rain and aerosol particle nucleation.
Current EPA methods for SO_2 measurement typically are fluorescence based and suffer from drift due to power fluctuations as well as interference from other organic molecules (aromatics) that can also fluoresce at UV wavelengths.

Experimental

The optical cavity was constructed using high reflectivity mirrors from Layertec (R = 99.9%), an LED centered at 308 nm (Rothner-Lasertchnik), with light collimated from the LED into the cavity and collected and focused onto a fiber optic (1um, Thorlabs) with an Avantes spectrometer used for light collection. The optics were mounted on a cage system consisting of 3 carbon tubes with 3D-printed components holding the mirrors and various other optics.

The mirror reflectivity was measured using the differential signals from He and N_2 caused by their different Rayleigh Scattering Cross-sections according to the following equation:

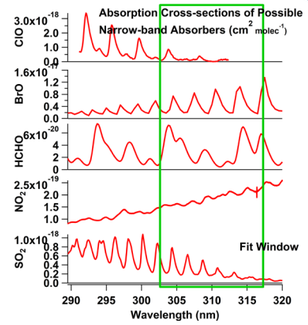
$$R(\lambda) = 1 - d_0\left(\frac{\frac{I_{N_2}(\lambda)}{I_{He}(\lambda)}\varepsilon_{N_2}(\lambda) - \varepsilon_{He}(\lambda)}{1 - \frac{I_{N_2}}{I_{He}}}\right)$$

Where d0 is the cavity length, I are the intensities in He and N_2 respectively, ε are the extinctions due to Rayleigh Scattering for N_2 and He respectively, all with respect to wavelength (λ).
SO_2 was supplied from a standard cylinder (AirGas) with a concentration of 10.14 ppm and diluted with zero air using a dilution calibrator. Measured SO_2 concentrations in the cavity were compared to a Thermo 43c SO_2 instrument which had been calibrated with the same set up.

Results

Possible Measured Species

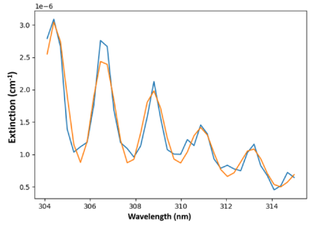
Because the BBCEAS instrument collects light over a range of wavelengths it is able to measure any narrow band absorbers in the range by Differential Optical Absorption Spectroscopy (DOAS) fitting. The figure at right shows a sampling of species including SO_2 that could be measured.

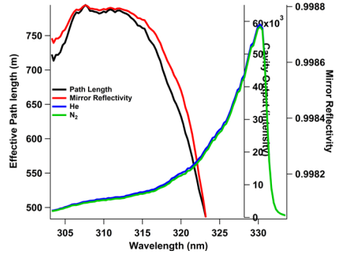


3D-printing Materials

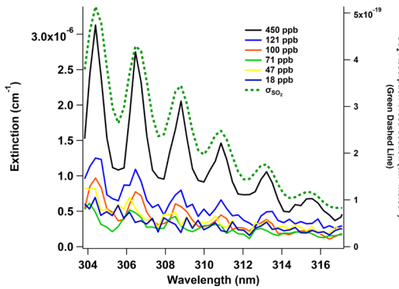
Two different 3D-printing materials were used for the components of the cage system: Acrylonitrile Styrene Acrylate(ASA) and Poly-Lactic Acid (PLA). All printed parts were printed on a budget Creality Ender 3 equipped with an updated hot-end (Micro-Swiss) that allowed for printing at higher temperatures. The mirror mount sections (ASA) were printed with 110% nozzle flow to minimize gaps and leaks since those sections would need to be air-tight. The mirror mounts were further acetone vapor smoothed to polish the finish and further seal the outer layer of plastic. The Teflon tube in the middle of the cavity was attached using fittings printed from ASA as well with the same settings and finishing. This printing process is still under testing to ensure the air-tight seal of the measurement cavity.
Structural parts and lens, fiber and LED holding parts were printed out of PLA due to the greater ease of printing this material and lack of a need for an air-tight seal.

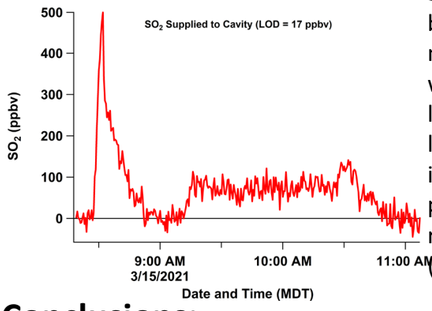
The measured mirror reflectivity was 0.9988 at 310.5 nm, giving a maximum absorbance path of 787 m.





Spectra were fitting using a custom Python fitting algorithm. A sample fit is shown at left.





Example spectra converted to extinction by the equation:

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right)\frac{1 - R(\lambda)}{d_0}$$

And then fitted to the absorption cross-section of SO_2:

$$\alpha(\lambda) = \sigma_{SO_2}[SO_2] + polynomial.$$

A range of concentrations were supplied to the instrument from dilution calibrator. Initial results show a background noise level between two signal averaged (5-10 minutes) references of 2 x 10^{-8} cm^{-1} which would indicate a detection limit of ~ 3 ppbv, while the noise level in the time series (lower figure) indicates a detection limit of ~15 ppbv. In RMS noise values, the references give an optical density (Beer's Law) of 2 x 10^{-3}.

Conclusions:

This work shows the proof of concept for a BBCEAS instrument for the measurement of SO_2 and other species of interest that also absorb around 308 nm. While the limit of detection does not currently compete with commercial instruments, further improvements can be made. Better filtering of the out of band light would allow for reduced noise (better use of the full well depth of the CCD relative to the read-out noise and dark current noise). The spectrometer used did not have a cooled detector, so longer integration times cannot be utilized to acquire more photons and also lower the limit of detection by spectral averaging. A more light efficient detector and better use of the detector range would enable an RMS noise level of 5 x 10^{-4} or lower which gets the instrument to a detection limit of less than 1 ppbv.

Acknowledgements:
This work was supported by a Utah Space Grant Consortium Faculty Research Seed grant.

References: see Thalman and Volkamer AMT 2010, Washenfelder et al. ACP 2008 and Langridge et al. Rev. Sci. Inst. 2008