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Reply on RC2

Ryan Thalman et al.

Author comment on "Detection of Sulfur Dioxide by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)" by Ryan Thalman et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-172-AC2>, 2021

Response to Reviewer #2

The authors thank referee #2 for the feedback given with regard to our paper "Detection of Sulfur Dioxide by Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS)". Below are specific responses to items raised in their general and specific comments.

"The detection limit (0.6ppbv) mentioned in the abstract is not obtained based on experiments but inferences, which is not acceptable. The measurement uncertainty is not mentioned and assessed. I encourage the authors to provide a more detailed characterization of this instrument and provide at least one measurement test to show the advantages of BBCEAS or its potential compared to the UV fluorescence method."

Further experiments have been carried out to assess the detection limit and measurement uncertainty as well as field applicability as described in the response to Reviewer #1. The results of these experiments are detailed in the revised version of the manuscript.

Major Comments:

Line 122, the LOD is obtained based on the measurement by Avantes? The plot of the time series of the baseline measurement should be presented rather than a value.

Because the Avantes proved so much worse in comparison with the Andor spectrometer/CCD combination, only the Andor data timeseries was shown. This is not unexpected as the Avantes spectrometer features a non-cooled detector, a high noise background, and an unoptimized slit resolution to wavelength range combination for this application. For the revision, all mention of the Avantes spectrometer has been removed to clarify the presentation of the results and focus on the optimal set up.

The measurement uncertainties are not discussed in the manuscript.

Discussion of measurement uncertainty is added to the section Noise Evaluation which includes discussion of absorption cross-section uncertainties and other measurement variables (uncertainty in R, etc). The measurement uncertainty is limited by the uncertainty of the reference cross-sections: 5% as given for the Rufus cross-section.

“In the paper there is no hint that the application of BBCEAS has a major advantage compared to other methods that are used for atmospheric detection of SO₂.”

We discussed other techniques in detail in the Introduction including interfering species specifically for fluorescence-based detection instruments. We have updated this section to add more details to this effect and elaborated the advantages of direct absorption measurements with DOAS analysis in the results and conclusion sections. The advantages of BBCEAS come with simplified light sources (LED compared to lasers or flash lamps), calibration standard free calibration, absence of interfering species, and long-term stability.

“The investigation of the applicability of the instrument in ambient air is missing”

Originally, ambient measurements were not completed due to the lack of variability of SO₂ in the vicinity of the locations of our testing (Richfield and Provo, UT, historical data for the last 6 months shows almost no measured concentrations in excess of 1 ppbv over that period). In response to the reviewers, ambient data was acquired to assess fitting of interfering species (such as NO₂) as well as performance in an ambient matrix. SO₂ was injected into the inlet line to provide varying SO₂ levels to measure. The description of these experiments was added to the Experimental, Results and Conclusion sections.

Field application should be added to prove the feasibility of this instrument.

A field application experiment has been added to the paper, with appropriate additions to the Experiment, Results, and Conclusions sections.

I believe the data used in Figure 6 was based on the time series from Figure 4, if the intercomparison measurement is conducted by 43c simultaneously, this plot can be revised as a scatter plot rather than used six average values. Even if the six points were used to do the intercomparison, the measurement error should be given.

The description of the calibration (intercomparison) experiment has been repeated and replaced with both data from a TECO 43i-TLE and the 43c instrument which were calibrated with the dilution calibrator. The real time data from these instruments is also incorporated and described for the ambient measurement comparison.

Why this instrument do not need the purge flow, are there some new designs of the construction of the cavity to protect the high reflectivity mirror, or some other reasons? Is the filter used in the experiment tests?

Several recent papers (Barbero et al., 2020, added to the instrument description) have described the lack of need for purge volumes in BBCEAS instruments. In this instance, a particle filter is always employed upstream of the cavity to remove deposition by particles on the mirror surfaces. In the current experiment no decay of the mirror reflectivity over time was observed to justify the added uncertainty (relative to sample length) and instrument complexity of purge volumes.

Technical Comments:

Line 29, second, and sec should be unified throughout the manuscript.

All instances of sec have been changed to second.

Figure 1, all the lines should be colored in black except BrO.

Figure 1 has been updated.

Line 109, how many hours rather than "several"?

The range was given because two separate experiments with different detectors were carried out. This has been clarified in the manuscript as the Avantes spectrometer data has been removed.

Line 106 lpm, please give the full name when first appear in the text.

The text has been updated.

Why other absorbers like HCHO, BrO are not considered in the spectrum fitting?

Other absorbers were not fit since only SO₂ was supplied in this experiment. Other species (NO₂) were included for the added ambient measurements. The relative strength of the differential absorption cross-sections of HCHO, BrO, and NO₂ relative to SO₂ in the wavelength range are: 0.69, 157, and 0.56 respectively. BrO is extremely short-lived and reactive, so it would not be detected in any of the configurations used in this work. While NO₂ can be detected, there are better cavity configurations and wavelength ranges with better detection limits (360 nm, 405 nm, 455 nm, etc.)

Line 120, so which one of the cross-sections is used in the instrument characterization in the following sections?

The text has been updated to read: "The Rufus et al. absorption cross-section was used for fitting because it yielded a 20% lower residual than the Bogumil et al. (2003) cross-section.

Figure 3, please label panel (A, B, C)

Figure 3 has been updated with panel labels.

Figure 4, please delete ":".

: has been deleted

Line 127, the integration time of 2 seconds is not consistent with that mentioned in Section 2.2.

The section has been updated to remove the discussion of the Avantes spectrometer.