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Atmospheric Measurement Techniques Discussions

Interactive comment on "Instrument inter-comparison of glyoxal, methyl glyoxal and NO_2 under simulated atmospheric conditions" *by* R. Thalman et al.

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Thalman et al. use results from two chamber studies (NCAR and EUPHORE) to compare the relative performance of nine instruments used to measure glyoxal and/or methylglyoxal. Glyoxal is measured by four main techniques: Visible Absorption Spectroscopy, Laser Induced Phosphoresence (LIP), Fourier Transform Infra-red spectroscopy (FTIR) and Solid Phase Microphase Extraction (SPME). Proton Transfer Reaction Mass Spectroscopy (PTR-MS) is additionally employed to measure methylglyoxal.

Thalman et al. showed good consistency between visible/IR reference cross sections and PTR-MS ion-molecule rate constants based on good agreement between the chamber measurement techniques that employed each separate calibration factor. They then compared seven instruments at EUPHORE to pure glyoxal/methylglyoxal mixtures, o-xylene and isoprene photoxidation experiments and ambient air. They found larger variability for measurement techniques that require external calibration or offline sampling. By systematically varying NO2 in the chamber, they were able to show cavity enhanced visible instruments are moderately impacted by NO2 interference, likely through wavelength dependent pathlength distortions. Finally they experimentally determined instrument limits of detection based on flushed chamber measurements.

Overall this paper fits well within the scope of AMT. As the authors note, the measurement techniques for detecting α-dicarbonyls have emerged very recently, providing ample need for an intercomparison. Their paper will be a useful resource for both instrument developers and users of their data. I recommend publication after the following comments are addressed.

1 Major Comments

- **Section 2.1.6:** How frequently was the CRDS calibration step employed for the Mad-LIP instrument? Should we expect drift in the calibration response factor from mirror alignment variations over the course of a single chamber experiment?
- **Section 3.2.1:** Do you know the cause of the second cluster of BBCEAS points offset from the 1:1 line Figure 3b (x-axis $>$ 1.5 ppbv)?
- **Section 3.2.1:** How well do the Mad-LIP/CE-DOAS slopes agree close to the start of the experiment? It would be interesting to know how well the Mad-LIP

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response is close to CRDS calibration to separate this from drift associated with mirror alignment changes.

- **Section 3.2.3:** The poor agreement between BBCEAS and CE-DOAS for methylglyoxal given the excellent agreement for stronger absorbers is interesting, given the similarity of the techniques. Past studies have shown that weak absorbers are highly sensitive to the spectral window chosen for analysis. The reported windows analysed by CE-DOAS and BBCEAS are 435-465 nm and 430-486 nm respectively, which could account for this discrepancy. Have the authors investigated sensitivity of fit window position to methylglyoxal?

- **Section 4.1:** I could not quite follow how the authors arrived at the recommended line strength values at the end of the section from the previous discussion. Could this be clarified?

- **Section 4.2:** Supplement, Line 81 - I was not quite sure how the 15% fit error for SCDgly was derived for the high NO2 case. Was it estimated from the fit residuals? How was the 10 ppbv threshold determined for when the NO2 pathlength distortion becomes significant? In principle it seems that the path length variations caused by the stronger absorber can be modelled. Is there also a possibility of other spectral effects at high concentrations (e.g. Raman "filling in" of NO2 absorption structures)?

- **Section 4.4:** A potential application of the α-dicarbonyl measurements is constraining high and low NOx VOC oxidation pathways, making the NO2 interference very relevant. It seems that the the dominant effect tested was pathlength distortion at very high NOx concentrations. Are you able to bound the associated interference at lower NOx levels (0-10ppbv) where reference cross section uncertainties are likely the dominant driver of interference?

- **Section 4.5:** Many previous modeling studies have compared simulation re-

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sults with glyoxal/methylglyoxal measurements derived from chemical derivitisation techniques such as DNPH-HPLC. The results of comparisons with SPME seemed highly variable relative to the spectroscopic techniques. In this paper, this was attributed to manual manipulation of samples. Does this problem apply more generally to the other chemical techniques?

- **Section 4.5** Instrument performance was generally assessed at relatively high glyoxal concentrations (up to 15 ppbv). Ambient levels (outside of heavily polluted regions) tend to fall in the range of 0-200 pptv. Do you have a sense of how much confidence we should have for measurements in this range based on the results of this study?
- **Section 5:** Could the authors clarify the basis of the conclusion for a lack of water vapour interference in point 5. It was not mentioned in the discussion section. Also it is not immediately obvious if it could be deduced based on the ambient air measurements in experiment E6, since the glyoxal concentrations could also be driven by many other confounding factors due to the uncontrolled nature of the experimental conditions.

2 Editorial Comments

- **Figure 4:** The right had side y-axis is missing a label
- **Figure 4 and 6:** I think a definition of what the error bars are is needed in the captions.
- **Figure S2:** The CE-DOAS points are a mixture of squares and circles. Is there a reason for this?

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 8581, 2014.