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Atmospheric Measurement Techniques Discussions

Interactive comment on "A two-channel, Thermal Dissociation Cavity-Ringdown Spectrometer for the detection of ambient NO₂, RO₂NO₂ and RONO₂" *by* J. Thieser et al.

Anonymous Referee #1

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Review of Thieser et al.

The authors report design and evaluation of a thermal dissociation cavity-ringdown spectrometer aimed at measuring ambient NO2, total PNs, and total ANs. They did extensive laboratory testing in conjunction with modeling to understand NO2 signal measured by CRDS and compared concentrations of NO2 and to other instruments sampling ambient air.

The paper is well written and organized. The modeling of the chemistry after thermal

dissociation is well thought out and valuable for anyone that does thermal dissociation measurements. Also, the authors demonstrate the model predicts the chemistry and is able to be used as a guide to interpreting field measurements. I recommend publication after attention to the comments below.

General Comments

1. Previous TD-CRDS instruments should be discussed and similarities/differences discussed more fully (Paul et al., 2009; Paul and Osthoff 2010; Thaler et al., 2011; Mielke and Osthoff 2012). The recent development of multiple CIMS approaches to measuring the major components of total ANs (e.g., Beaver et al., 2012) should be mentioned.

2. The paper should explain the motivation for lasers at two different wavelengths and address any additional complexity associated with this choice?

3. The paper should explain the choice of operating pressure, since that affects the TD signals and is presumably a parameter that could be optimized to improve specificity of the measurements.

4. The authors are correct that pyrolysis of O3 was not important for Day et al. (2002) since the residence time in that instrument was short. In Lee et al. (2014), the authors demonstrated that at long enough residence time, pyrolysis of O3 becomes sufficient to become a positive interference in the total ANs channel. Where does the TD-CRDS fall in these two regimes? Also, was pyrolysis of O3 tested at all or just calculated? The negative ANs in the field might be an indicator of an O3 effect.

5. The authors demonstrated that the temperatures selected fully decompose total PNs and total ANs and the temperature selected for total PNs does not decompose any total ANs. Were any experiments conducted to determine if any HNO3 is decomposing at the temperature selected for total ANs?

6. It seems likely that a fuller suite of PNs were measured by TD-CIMS? A direct

comparison of totals or scaling of the PAN by the measured ratios would seem a better approach.

7. The interpolation necessary to measure total ANs can be affected by atmospheric variation on the measurement time scale. Perhaps a strategy for assessing maximum variability in the underlying NO2 or SPNs would be useful?

8. Some additional comments on the transmission of sticky molecules from the inlet through the sampling system would be useful. Would isoprene hydroxynitrates, ClNO2 or HNO3 reach the heater without losses?

Specific Comments 1. Page 11534, line 17 – “nutrient” should be “nutrients”

2. Page 11535, line 17 – For upper tropospheric measurements of HO2NO2 and CH3O2NO2, other references are missing, including Murphy et al., 2004, Kim et al., 2007, and Nault et al., 2015.

3. Page 11535, line 19-20 – The authors are correct that near the surface of the planet, thermal decomposition is the most important loss rate; however, at higher altitudes, photolysis and reactions with OH dominate.

4. Page 11537, line 19-20 – Please define delta and be consistent with its use throughout the entire paper.

5. Page 11540, lines 7-8 – Any experiments to determine if multifunctional nitrates are filtered out as well?

6. Page 11563, lines 24-26: Where does correction factor maximum uncertainty of 30% come from?

7. Page 11564, lines 20-21: can you state what the certain conditions are?

8. Figure 6 caption – how much O3 was present during the experiments?

9. Page 11586, Figure 8: If poor fit is caused by problem with PAN mixing ratio during

experiment, why not repeat experiment?

10. Page 11588, Figure 10: Figure legend is too small.

11. Page 11591, Figure 13: Figure legend is too small.

12. Figure 18 caption – what are the green points? May also want to reconsider colors and descriptions for colors since the reader may think any black data points are uncorrected data, including for NO2, which the reader could interpret to mean the NO2 measurements would need corrections.

âĂČ References:

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Interactive comment on Atmos. Meas. Tech. Discuss., 8, 11533, 2015.