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Atmospheric Measurement Techniques Discussions



# *Interactive comment on* "High concentrations of $N_2O_5$ and $NO_3$ observed in daytime with a TD-CIMS: chemical interference or a real atmospheric phenomenon?" *by* X. Wang et al.

**Anonymous Referee #1**

Received and published: 14 September 2013

General Comments:

This paper describes measurements of NO3 + N2O5 in a dense, urban area of Hong Kong. The paper reports the unusual occurrence of daytime peak signals for these compounds, which are normally present at much larger concentrations at night. However rather than focus on the scientific implications of this finding, the paper primarily discusses the potential for measurement artifacts with a chemical ionization mass spectrometer (CIMS) that can lead to artificially high daytime NO3+N2O5 signals. The paper quantifies several interferences and concludes that the most severe is that due to the interaction of PAN and NO2 within the instrument or its inlet. Daytime N2O5



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signals are attributed partially to the interference signal, and partially to a real daytime maximum in NO3+N2O5.

In general, the consideration of interferences for measurements at 62 amu using I- reagent ion in the CIMS is a useful contribution to the literature. Prior reports have indicated the utility of this mass for detection of the sum of NO3 + N2O5. Although some more recent papers have suggested that the cluster ion (I- N2O5) is more specific, it is worthwhile to have an understanding of potential artifacts at the NO3- mass. In particular, the interaction of PAN with NO2 has not been previously considered as an interference, and is a new contribution to the literature. As such, I recommend publication in AMT subject to some minor comments.

The two general comments for revision are as follows: First, the paper lacks some detail that would be useful in understanding the measurements and the potential for real daytime maxima in N2O5, which are inferred in the paper. The daytime steady state in NO3+N2O5 is straightforward to calculate. See, for example, Geyer 2003 (Geyer, A., et al., J. Geophys. Res., 108, doi: 10.1029/2002JD002967, 2003) or Brown 2005 (Brown, S. S., et al.: J. Photochem. and Photobiol. A, 176, 270-278, 2005.). The calculated daytime steady states should be plotted together with the case studies in Figure 4. That would give some since for how unusual the daytime measurements really are and the level of the predicted N2O5 signal relative to the measured one. Second, the calibration scheme should be described in somewhat more detail, graphically if possible. The authors should more explicitly consider whether there is any potential for errors in the gas phase calibration scheme to explain any remaining discrepancy between the predicted and measured daytime NO3 + N2O5.

Specific Comments and technical corrections:

Page 7475, line 18: Suggest removing the word “emerged”

Page 7475, lines 28-89 – page 7476, lines 1-2: There is no comparison between CRDS and CIMS instruments in the Slusher 2004 reference, although there is one given in



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the Chang 2011 reference.

Page 7478, line 9: Figure 3 erroneously referenced. There does not appear to be a figure showing the mass spectrum in this paper.

Page 7478, line 27: Figure 4 also incorrectly referenced. The actual figure appears to be figure 5.

Page 7478, last paragraph: The NO3 + N2O5 calibration technique is critical to the arguments about daytime N2O5 and warrants a figure. A demonstration of an example calibration (e.g., counts at 62 amu plotted against titration of NO2, O3 or both from the calibration source) would be helpful to demonstrate the stated 3% accuracy of the measurement.

Page 7481, line 8: The definition of "ambient" signal is not clear – all signals are recorded during sampling of ambient air, presumably. Suggest referring to this as the "total" signal, or the "total signal in ambient air."

Page 7481, line 18-20: The association between PAN and greater than calculated daytime N2O5 in the Brown and Osthoff studies is not necessarily related to the potential for PAN interference on the CIMS, since the cited studies use a different detection principle (CRDS). The authors should add a sentence to this effect.

Page 7481, bottom: Should there be a reference to figure 6 somewhere in this text?

Page 7482, line 5: Suggest rewording: "23 $\pm$ 4 pptv of apparent NO3+N2O5 signal per ppbv of PAN"

Page 7482, line 11: Suggested wording: "The mechanism for the interference of PAN on the NO3- signal is unclear."

Page 7482, line 16: Figure 6 called out after Figure 7.

Page 7483, line 2: Specify which section of the paper will have the analysis of the PAN interference (rather than "later").



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Page 7483, line 4: Delete “the” before HNO3.

Page 7485, line 10: “are” instead of “were”.

Page 7485, line 16: Delete the word “by”

Page 7486, line 8-9, and Figure 9: It would be helpful to have the data for NO, NO2, O3 and PAN together with the measured N2O5 to understand how close to the predicted daytime steady state these measurements are.

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Interactive comment on Atmos. Meas. Tech. Discuss., 6, 7473, 2013.