

***Interactive comment on “Chlorine activation by
 N_2O_5 : simultaneous, in situ detection of ClNO_2 and
 N_2O_5 by chemical ionization mass spectrometry”
by J. P. Kercher et al.***

Anonymous Referee #2

Received and published: 28 February 2009

General Comments:

This paper describes a technique for simultaneous in situ monitoring of ClNO_2 and N_2O_5 by chemical ionization mass spectrometry. Accurate concentrations of these species are necessary to better understand activation of chlorine in the troposphere. Though a preliminary comparison of CIMS and CaRDS measurements of N_2O_5 is in the literature (Huey, Mass Spectrometry Reviews, 2007, 26, 166-184) the authors have completed the necessary calibrations to validate the CIMS N_2O_5 data. The authors have carefully evaluated their technique and clearly present their findings in this manuscript. I only have a few minor questions regarding the material in the manuscript.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Specific Comments:

Section 4.1 pg 127 line 16. Due to the variation in sensitivity as a result of internal and external factors, were calibrations conducted at varying times of day?

Section 4.1 pg 129 line 2. While the information on future N₂O₅ field calibrations is interesting and the new direction is worth mentioning, it seems the details are better suited to a manuscript that employs the technique.

Section 4.1 pg 129 and Figure 3. The section describing the ClNO₂ calibration is a bit confusing. It is stated on pg 129 line 16 that ClNO₂ was calibrated by passing a dry flow of N₂ containing a known amount of N₂O₅ over a wet NaCl bed. However, the inset of Figure 3 is described as the response to N₂O₅ in a flow of ambient air at approximately 20% RH (pg 129 line 22). Please clarify the conditions (i.e. dry N₂ or ambient air) for the ClNO₂ calibration. Also, it seems misleading in Figure 3 to plot ClNO₂ counts as a function of N₂O₅ concentration. Because the N₂O₅ signal in the inset does not decrease to zero upon exposure to the salt bed, shouldn't the ClNO₂ counts be plotted against the change in N₂O₅ concentration or ClNO₂ concentration as mentioned on pg 129 line 23? Lastly, the scale for the ClNO₂ counts in the main plot of Figure 3 seems inconsistent with the inset. It appears that a calibration where the wet salt bed is exposed to 1.5 ppbv N₂O₅ yields approximately 3000 Hz for ClNO₂, but the scale in the main plot does not exceed 2500 Hz. Again, please simply clarify what is being represented by the ClNO₂ trace in the main plot.

Section 4.2.1 and Figure 4 discuss the anion signal dependence on IMR water partial pressure. What concentrations (p 130 line 21) of ClNO₂ and N₂O₅ were used to generate the data in Figure 4? Is the correlation between anion signal and water partial pressure consistent for typical ambient concentrations of ClNO₂ and N₂O₅?

Section 4.2.1 pg 131 line 13 the authors state that I⁻ and [I(H₂O)]⁻ are the most important reagent ions and Figure 4 pg 148 helps to illustrate this point. However in section 4.5 pg 135 line 12 it is stated that on shorter timescales the signal is normalized to the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



total I- and $[(\text{H}_2\text{O})_2]$ - clusters. Why is the signal normalized to $[(\text{H}_2\text{O})_2]$ - instead of $[(\text{H}_2\text{O})]$ -?

Section 5 pg 137 line 17. Detailed information is given for the ship track from 19 March through 22 March, but Figure 6 begins on 22 March. What are the locations of the ship and the anticipated source regions of ClNO_2 and N_2O_5 through 24 March? Also, is it possible to include the wind direction (or some indication of location or source region) in Figure 5 pg 150? Given the units for time (Fraction DOY/UTC), it would also be helpful to include an indicator of time of day.

Figure 6 page 150. Please double check the spelling of 'ratio' on your y-axis.

Section 5 pg 138 line 9. Please consider reporting the temperature in Kelvin for ease of comparison to the value presented in section 4.3 pg 132 line 20.

Summary:

The authors have very clearly shown their capability of employing chemical ionization mass spectrometry to simultaneously monitor ambient concentrations of N_2O_5 and ClNO_2 . The significance of the work, quality of science and quality of presentation are all excellent.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 119, 2009.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)