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Atmospheric Measurement Techniques Discussions

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 #1

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This paper describes a new analytical method for simultaneous speciated measurements of the atmospheric trace gases N2O5 and ClNO2 and its atmospheric deployment on a research ship. Atmospheric ClNO2 can be formed via heterogeneous reaction of atmospheric N2O5 with chloride containing solutions and solids. Processes involving N2O5 and ClNO2 have an influence on NOx, which in turn impacts ozone. Therefore atmospheric N2O5 and ClNO2 measurements are important. The new method presented represents a special form of CIMS where hydrated I- ions (I-Wn; W=H2O) are used as reagent ions. The CIMS-method is thoroughly described and its use for atmospheric measurements has been convincingly demonstrated.

Therefore the paper is certainly **well suited for publication in AMT** after **some revision**.

My recommendations are as follows. Comments concerning technical details will be given separately (copy of the draft).

1. The product ions I-N2O5 and I-ClNO2 suffer from dissociation in the CDC which requires sufficient lowering of the electric field in the CDC. This has been mentioned by the authors. However in addition a figure should be added demonstrating this undesired perturbing effect.

2. The accuracy and precision need to be discussed more thoroughly. In particular uncertainties introduced by uncertainties of the calibration techniques should be addressed in more depth. Considering the complex calibration the accuracy given seems somewhat optimistic. Therefore a more thorough discussion is needed if you want to really convince the reader.

3. Are the percent numbers given for accuracy and precision plus and minus ?

4. Figure 1 should contain a more detailed description of the ion source and ion reaction region.

5. At least one full mass spectrum should be shown. It will allow the reader to see possibly present additional reagent ions and product ions.

6. The strong increase of the product ions I-N2O5 and I-ClNO2 with increasing water vapour in the reaction region is interpreted by the authors as an increase of the N2O5 and ClNO2 reactions of I-Wn with increasing n. However, it is at least conceivable that hydration of the product ions may also have some role. Hydrated product ions may be less affected by loss of N2O5 and ClNO2 during passage of the CDC since H2O ligands may boil off first. Do you see hydrated product ions

AMTD

2, S24–S26, 2009

when lowering the electric field in the CDC ? Did you vary the E-field for different water vapour pressures ?

7. The sampling system used during the ship-cruise should be shown as an additional figure.

8. The procedure of frequent cleaning of the sampling line should be described.

9. The authors mention that during the ship cruise the measured product ions with mass numbers consistent with I-Cl “did not demonstrate the expected Cl isotope ratio”. More precise information should be given and possible cuses should be discussed.

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