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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.

J. P. Kercher et al.

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We thank Reviewer 1 for the helpful and insightful comments. We believe our responses to these comments have improved the manuscript considerably.

Reviewer #1: 1. The product ions IN2O5 and IClNO2 suffer from dissociation in the CDC which requires a lowering of the CDC electric field. A figure should be added demonstrating the undesired perturbing effect.

We have added a figure as requested. We would like to point out that the CDC electric field strength can easily be optimized for the detection of cluster anions, ie I(ClNO2) and I(N2O5) in that there are not undesirable perturbing effects by the CDC which are detectable. It is certainly possible that the electric field strength of the CDC could be

such that the clusters are undetectable, as is likely in some existing CIMS instruments. The text has been updated to clarify this point.

2. Discuss the accuracy and precision more thoroughly.

We have enhanced our discussion of accuracy and precision in the revised manuscript. In particular we have listed many sources of inaccuracy and have also discussed how we minimize most of them. We still conclude that the independent deployment of the CIMS instrument would have an uncertainty of +/- 20% deriving from the calibration source. For precision, we would prefer to have an in situ test that demonstrates, for constant atmospheric concentrations, the precision is equal to that predict from Poisson statistics. However, we have yet to sample a suitably constant N2O5 mixing ratio and simply provide a reference that shows we have demonstrated counting error dominated precision for other species, see Wolfe, 2007.

3. Are the percent numbers +/-?

Yes, the percent uncertainties are +/-, we have clarified this in the text.

4. Figure 1 should have a more detailed description of the ion source and IMR.

Figure 1 has been updated to include the ion source and the sampling system used during a ship-deployment as requested later in comment 7.

5. At least one full mass spectrum should be shown so the reader can see other reagent and product ions.

A mass spectrum has been added and the text has been updated.

6. Do you see hydrated product ions when lowering the electric field in the CDC?

Hydrated product ions, such as NO3(H2O) are observed given sufficient water vapor in the sampling stream. IClNO2(H2O)n and IN2O5(H2O)n clusters are not observed. The text has been updated to reflect this.

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7. Show a figure of the sampling system used on the cruise.

The sampling configuration used while on board the R/V Knorr has been added to Figure 1 and the text has been updated.

8. Describe the cleaning of sample tubing.

The text has been updated to describe the cleaning process.

9. Describe and discuss the possible causes for why the ICl isotope ratio did not match the known Cl ratio.

The ICl isotope ratio was biased to the 37Cl isotope, indicating an interfering ion present at m/z 163.9. This impurity is a gas phase species which is ionized by Iodide reagent ions or some other trace ion in the system (e.g. NO3-, O2-), but currently we have not identified the species. This section has been updated in the text. It may be possible to measure ClNO2 as the I35Cl anion, especially in laboratory settings, but the uncertainty in field measurements would be larger than we report here due to the lack of agreement in the isotopologue signal.

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