

Interactive comment on “Measurements of HNO₃ and N₂O₅ using Ion drift – Chemical Ionization Mass Spectrometry during the MCMA – 2006 Campaign” by J. Zheng et al.

J. Zheng et al.

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We have addressed the comments regarding writing style and grammar in the revised manuscript. The specific scientific comments are responded below.

1) I am surprised at the low levels of HNO₃ observed in the campaign. It would be interesting to compare HNO₃ (or total nitrate) production rates during the day from NO₂ reacting with OH to observations. This would give some insight into lifetimes and be a check on the consistency of the data.

We have calculated the HNO₃ production rate on March 20, when OH, NO_x, HNO₃, PBL, and aerosol nitrate were measured. The results indicate the total HNO₃ (sub-micron aerosol nitrate + gaseous HNO₃) cannot account for all the HNO₃ produced

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from OH + NO₂ reaction. Heterogeneous reaction of HNO₃ on dust surfaces has been shown to be important during MILAGRO, leading to permanent removal of HNO₃ to form non-volatile mineral nitrates such as Ca(NO₃)₂ (Querol et al., 2008; Fountoukis et al., 2007; Hodzic et al., 2007). Querol et al. (2008) estimate the fraction of total nitrate at T0 in the PM₁₀ – PM_{2.5} range as ~20% of the total nitrate, with a higher fraction in the early part of MILAGRO due to reduced precipitation and increased dust concentration. If the dust size distribution in Mexico is similar to that reported by Maring et al. (2003) and the dust reactivity is uniform across the dust size distribution, this size range would account for about ~1/3 additional dust nitrate beyond that PM₁₀-PM_{2.5} size range. With all supermicron aerosol nitrate considered and using a calculated dry deposition rate according to Fast et al. (2006), which is consistent with literature values (Myles et al., 2007; Pryor and Klemm, 2004), about 77% of HNO₃ production can be accounted for. A gap of 23% is well within the experimental uncertainties.

2) “The comparison between the ID-CIMS and the ICMS really doesn't look that great. If you were to remove the four highest points on the graph (which largely control the correlation coefficient) above 1.2 ppbv there doesn't seem to be much correlation. This should be addressed as the data seems to be scattered and there is little evidence for a bias in one direction. Is this due to detection limit issues? By the way detection limits are stated for the ID-CIMS but I am not sure how they are derived this should be fixed.”

The ICMS data time resolution is on the order of hours. Therefore, each data point in Fig. 10 represents averaged data collected by the ID-CIMS in two to four hours. This also makes the data points scarce in Fig. 12. We also have added error bars for the ID-CIMS data points to indicate the variation of HNO₃ during the average time period. The detection limit of the ID-CIMS was determined from the standard deviation of the background signals, which were measured by passing air sample through NaHCO₃ coated nylon cloth. When the background signal was collected for longer than 2 min, we found its standard deviation was fairly reproducible. Thus we reported a fixed value.

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3) A lot of time is spent on how the ID-CIMS sensitivity can be calculated. However, as stated there are a lot of parameters used each with its own level of uncertainty. The comparison of the calibration to this calculation indicates that this can be off by more than a factor of two (for HNO₃) and 50% for the N₂O₅. So I am not there is that much utility to these calculations as you can probably guess the expected sensitivity reasonably well with some knowledge of the ion molecule rate constant and an estimate of the reaction time. For this reason, I question the inclusion of this lengthy section of the paper (much of sections 2.1 and 2.2). You could cut it out and describe the calculations and nothing would be lost. If this section is not cut some justification for its inclusion should be added. For example, a comparison of the calibration and calculations and a discussion of why they are different. However, I suspect all you are finding out is that HNO₃ is easily lost in the instrument.

As the referee suggested, we agree to reduce the length of the experiment section. We have moved part of the experiment section into Appendix A, which describes the theoretical work to obtain reduced ionic mobility of the reagent ions. This is the first time when the ID-CIMS was deployed in the field work. Thus we try to establish the unique working principle of the ion-drift CIMS. It is true that the ion-molecule reaction products can be estimated in any CIMS configurations. However, inside the ID-CIMS, the ion trajectory is much more regulated and ion diffusion or discharge loss can be minimized by the electric field generated inside. Thus the ion-molecule reaction can be more accurately quantified from the ion speed and the reaction length. This is especially useful when the analyte standards cannot be easily obtained during the field campaign, e.g. N₂O₅. The factor of 2 between the calculated concentration and the volumetrically determined concentration of HNO₃ and N₂O₅ standards is a system-dependent parameter, which is a constant given certain reaction temperature, pressure, and the transmission efficiency of the mass filter. This factor was found very reproducible during extensive laboratory calibrations. The reduced mobility of SiF₅⁻ and I⁻ anion are critical to determine the ion-molecule reaction time and were not reported in any literature. We believe it is important to accurately estimate them

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through ab initio calculations.

The HNO₃ is hard to sample and we agree that our inlet system was not perfect. We experimented with smaller diameter tubing but the drift tube pressure dropped significantly, which cause deterioration in sensitivity. Thus the inlet was a tradeoff between minimizing surface effects and improving instrument performance.

4) My final comment is the inclusion of the N₂O₅ results. I think a better case needs to be made that the observed signal is indeed N₂O₅. I- could react with many things in the Mexico City atmosphere such as PANs to give some NO₃- signal. This section should be pulled out or calculations using the N₂O₅ equilibrium constant and observations of NO₂ and ozone to see if these levels are at least feasible in this warm environment.

In response to the N₂O₅ data verification, we noticed that I- reacts with both NO₃ radical and N₂O₅ to produce NO₃-. PANs will also react with I-, however the products are carboxylate ions (Slusher et al., 2004). During this N₂O₅ episode, the ambient temperature was between 18 and 13 °C and more than 25 ppb NO₂ was present. Under thermodynamic equilibrium, NO₃ should be less than 4% of the total signal. Thus we are confident the signal was from N₂O₅.

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