

Interactive comment on “Measurement of HONO, HNCO, and other inorganic acids by negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS): application to biomass burning emissions” by J. M. Roberts et al.

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We thank the reviewers for their comments. The two general points raised by the reviewers are well taken; (1) the magnitude and origin of background signals on the ions of interest are a major concern in a measurement of this kind, and (2) decomposition of larger ions could lead to signals at masses of interest. We consider our work to be an initial assessment of these effects and others in the NI-PT-CIMS, and as one of the reviewers noted, most relevant to the work we present on biomass burning (BB) measurements. The application of our method to ambient air measurements requires

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further improvements and an increased understanding of these issues.

The background levels in the NI-PT-CIMS system as deployed in the BB measurements had several sources. There appears to be material on the walls of the ion flow tube that adds to the background at any given time, and can be accounted for by a proper gas phase zero. The acetic anhydride source needed to be replenished every several days or so. In the BB experiment, this involved opening that part of the system to room air, which resulted in an increase in the backgrounds of the major ions. These aspects of the system will be emphasized in the final paper and several steps to improve operations suggested. Specifically, a heated flow tube and an improved acetic anhydride introduction apparatus will be recommended. Some minor fragmentation of large organic acids was observed in the first paper on NI-PT-CIMS (Veres et al., 2008), so we acknowledge that this can be a problem, however, most proton transfer reactions between acetate and other organic acids are quite modest energetically, making this a fairly “soft” ionization technique. The HNO₃ to nitrite fragmentation that we looked at in this work is a more likely possibility based on the thermochemistry, and was at most a few percent pathway.

The specific suggestion of addition of NH₃ to the system to reduce backgrounds, as described by Huey et al., (Huey et al., 1998) and Neuman et al., (Neuman et al., 2002), is a possible solution to the high background of nitrate ions, since NH₃ appears to react with surface-adsorbed nitric acid to prevent it from desorbing into the gas phase. However, preliminary work by one of our co-authors (J.A. Neuman, personal communication) with the SiF₅⁻ CIMS, indicated that NH₃ addition slows the response time to formic acid in that system. We interpret this to be a result of surface NH₃-HC(O)OH complexes that are still partially volatile. A complete assessment of NH₃ addition for the NI-PT-CIMS is beyond the scope of this paper and awaits further work.

The acetic anhydride source used in this work consisted of a small volume (30 cm³) bubbler through which a small flow of the source N₂ (1.5 SCCM) was directed. The gas stream was assumed to be saturated at the vapor pressure of acetic anhydride at

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the exit of the bubbler (4 Torr at 25C), and that flow combined with the total N2 flow (2 SLPM) resulted in an estimated acetic anhydride mixing ratio of 4 ppm.

The typo found by Reviewer #2 is acknowledged and corrected in the final version.

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