

Interactive comment on “Using collision-induced dissociation to constrain sensitivity of ammonia chemical ionization mass spectrometry (NH_4^+ -CIMS) to oxygenated volatile organic compounds” by Alexander Zaytsev et al.

Anonymous Referee #1

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This manuscript presents the development and characterization of a TOF-CIMS that can be operated in either ammonium (as NH_4^+ -CIMS) or hydronium (as PTR-MS) ion modes. The sensitivities and detection limits of NH_4^+ -CIMS mode of the instrument are probed for a number of oxygenated volatile organic compounds (OVOCs). A declustering scanning procedure based on collision-induced dissociation of reagent ion-analyte adducts is used to constrain the sensitivity of NH_4^+ -CIMS to a wide range of OVOCs for which no calibration standards exist. Application of this procedure for measurements of the composition of secondary organic aerosols is demonstrated using laboratory ex-

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periments of 3-methylcatechol photooxidation. This manuscript is well-written and provides useful information on the nature and sensitivity of the NH_4^+ ionization method that is shown to be promising for measurements of a wide range of oxidized organic compounds in both gas and particle phases. I recommend for this manuscript to be published in Atmospheric Measurement Techniques after the authors address several important concerns as detailed below.

P5, L15-16. The authors stated that organic compounds with lower sensitivities under dry conditions exhibit a stronger humidity dependence and that higher molecular weight molecules show a weaker humidity dependence. It would be interesting to plot the sensitivity of calibrated compounds versus their molecular weight to check if there is a clear relationship between sensitivity and molecular weight. It is also interesting to check if there is a connection (relationship) between water dependence and V_{50} or KE_{cm50} values for OVOCs.

P5, L18. Are there any evidence for protonated ions of organic molecules, especially for aerosol samples?

P6, L25-28. What are the RH conditions for the measurements presented in Fig. 4? Is the relationship between the KE_{cm50} and sensitivity of calibrated compounds probed under varying RH conditions? Given that the sensitivity of NH_4^+ -CIMS greatly depends on RH (Fig 2), the relationship between the KE_{cm50} and sensitivity may also be RH dependent. This issue merits additional discussions in the manuscript, as it determines whether the relationship obtained at a certain RH can be applied to measurements performed at a different RH.

P6, L33. It is not clear how the reaction time in the reaction chamber was determined based on the sensitivities observed in H_3O^+ mode. An elaboration about this should be included in the manuscript.

P7, L2-4. Again, is there a RH dependence of the kinetic sensitivity or the maximum sensitivity of NH_4^+ -CIMS?

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P7, L20. Can the sensitivity of H_3O^+ reagent ions to acetone represent the sensitivities to other OVOCs? Did the authors make any measurements and comparisons of sensitivities in H_3O^+ mode for different calibration compounds as listed in Table 1?

P7, L24–26. Similar or relevant observations about the sensitivity and selectivity of NH_4^+ and H_3O^+ reagent ions have been reported in previous studies. For example, Aljawhary et al. (2013) showed that $(\text{H}_2\text{O})_n\text{H}^+$ reagent ions are more selective to organic compounds with lower oxygen content. Zhao et al. (2017) showed that NH_4^+ reagent ions are sensitive to a wide range of oxidized organic compounds including highly oxygenated and higher molecular weight molecules formed from ozonolysis of alpha-pinene. The findings in these studies should be discussed in relation to the current work.

P8, L7. Since the authors never discuss the third ion source in the manuscript, I would suggest removing the statement “the instrument is equipped with three corona discharge ion sources”.

Table 1. The detection limit is usually defined as the concentration that gives rise to a signal of 3 sigma. I wonder why the authors use 2 sigma.

References:

Aljawhary, D., Lee, A. K. Y., and Abbatt, J. P. D.: High-resolution chemical ionization mass spectrometry (ToF-CIMS): application to study SOA composition and processing, *Atmos. Meas. Tech.*, 6, 3211–3224, 2013.

Zhao, Y., Chan, J., Lopez-Hilfiker, F. D., McKeown, M. A., D'Ambro, E. L., Slowik, J. G., Riffell, J., and Thornton, J. A.: An electrospray chemical ionization source for real-time measurement of atmospheric organic and inorganic vapors, *Atmos. Meas. Tech.*, 10, 3609–3625, 2017.

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