

# ***Interactive comment on “Using collision-induced dissociation to constrain sensitivity of ammonia chemical ionization mass spectrometry (NH<sub>4</sub><sup>+</sup>-CIMS) to oxygenated volatile organic compounds” by Alexander Zaytsev et al.***

**Anonymous Referee #1**

Received and published: 7 January 2019

This manuscript presents the development and characterization of a TOF-CIMS that can be operated in either ammonium (as NH<sub>4</sub><sup>+</sup>-CIMS) or hydronium (as PTR-MS) ion modes. The sensitivities and detection limits of NH<sub>4</sub><sup>+</sup>-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<sub>4</sub><sup>+</sup>-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-

[Printer-friendly version](#)

[Discussion paper](#)



Interactive  
comment

periments of 3-methylcatechol photoxidation. This manuscript is well-written and provides useful information on the nature and sensitivity of the  $\text{NH}_4^+$  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  $\text{KE}_{cm50}$  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  $\text{KE}_{cm50}$  and sensitivity of calibrated compounds probed under varying RH conditions? Given that the sensitivity of  $\text{NH}_4^+$ -CIMS greatly depends on RH (Fig 2), the relationship between the  $\text{KE}_{cm50}$  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  $\text{H}_3\text{O}^+$  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  $\text{NH}_4^+$ -CIMS?

Printer-friendly version

Discussion paper



P7, L20. Can the sensitivity of  $\text{H}_3\text{O}^+$  reagent ions to acetone represent the sensitivities to other OVOCs? Did the authors make any measurements and comparisons of sensitivities in  $\text{H}_3\text{O}^+$  mode for different calibration compounds as listed in Table 1?

P7, L24-26. Similar or relevant observations about the sensitivity and selectivity of  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  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  $\text{NH}_4^+$  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.

---

Interactive comment on *Atmos. Meas. Tech. Discuss.*, doi:10.5194/amt-2018-425, 2018.

Printer-friendly version

Discussion paper

