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Atmospheric Measurement Techniques Discussions

Interactive comment on "Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts" *by* F. D. Lopez-Hilfiker et al.

Anonymous Referee #2

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This paper describes sensitivity determination for the UW iodide HrTOF-CIMS with FIGAERO inlet. The results of this study can be used to provide the upper limit of the instrument sensitivity for a class of highly oxidized organic compounds, which are not known in molecular structures or even in functional groups. The authors conducted calibration of N2O5 detection with iodide-adduct HrTOF-CIMS to derive the highest sensitivity – collision limited, using independent absorption method. Then by changing the electric field between two electronic lenzes, they monitored the declustering of

adduct ions from relevant product ion distributions. By applying this method to other organic compounds, they conclude that N2O5 and all these organic compounds react with iodide at collision-limited ion-molecule reactions. But some of the adduct products are declustering. The electric field applied for declustering is related to the binding energies of adducts, which determines CIMS sensitivities, by affecting transmission efficiencies..

The statement that organic compounds tested in this study all react with iodide at collision-limit quite trivial. It is well known that ion-molecule reactions take place in collision limited reaction rates, which are all close to 1-2e-9 cm3 s-1, very little dependent on molecules (size and shape; only has 30% changes in reaction rate), as also discussed in [Erupe et al., 2011]. That means, by simply using this 2e-9 cm3 s-1 reaction coefficient, one can estimate CIMS's highest sensitivity of 20 Hz per ppt reactant per million Hz reagent ions using the ion-molecule reaction time used in this specific CIMS in this study. Similarly, we can also apply this method is to other CIMS, including CI-Api-TOF, with known ion-molecule reaction times. This application, however, is only valid with extremely low background ion signals of reactants. Therefore, experimentally demonstrating that these large highly oxidized organic compounds can be estimated with this upper limit of sensitivity is an important contribution to ELVOC and HrTOF-CIMS community.

Minor comments:

Page 10876: Line 26, please include You et al. ACP 2014 and Yu and Lee EC 2012 [You et al., 2014; Yu and Lee, 2012] – they are quire relevant to this study in terms of discussing the deviation of actual sensitivities from the collision-limited sensitivity.

Page 10877: Lines 9-10: Good selectivity is an advantage, for most CIMS, except CI-Api-TOF and the current UW CIMS that measures hundreds of different compounds together.

Line 10-13: Not measuring molecular structure is not unique to CIMS. This is a general

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issue for all mass spec techniques, unless tandem analysis is used.

Line 26-29: Experimentally determine “the relative strength of bindings of clusters” (rather than effective binding energies) . . . dV50 (volts) is an electric potential difference and is not energy (j or cal).

Page 10884: Line 20: What is needed for DFT calculations is cartesian geometries, rather than functional groups and molecular structures. Although, the half of the statement is correct.

Figure 5 results: please show the detailed list of specific CxHyOzN0-1I- compounds. Did you include C5 and C9+C10 together? Can you discuss more relative difference C5 vs. C9+10 and in Alabama vs Hytiala? What can you say with the comparison of sub-micron size of organic aerosol (derived from AMS) with your measurements – are they really related to each other – physically? I would remove AMS data here which does not bring any new information regarding the main conclusion of the paper but rather more confusing with that.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 10875, 2015.