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Atmospheric Measurement Techniques Discussions

Interactive comment on "Chemistry of α-pinene and naphthalene oxidation products generated in a Potential Aerosol Mass (PAM) chamber as measured by acetate chemical ionization mass spectrometry" *by* P. S. Chhabra et al.

Anonymous Referee #1

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This manuscript describes the use of the newly developed acetate chemical ionization mass spectrometer to study atmospheric oxidation products. Using an acetate ion source, the authors are able to measure comprehensively organic acids from two model SOA systems. With the high-resolution time-of-flight mass spectrometer, elemental formulas of the acids, and bulk chemical properties, such as O/C, H/C, number of carbons, vapor pressure, are calculated.

My major concern is whether AMT is a good fit for this paper, because it focuses more

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on application of new techniques to study atmospheric systems, rather than development of a new instrument or methodology (see comment below). I will leave it up to the editor to decide whether this manuscript fits the scope of AMT. Otherwise, the data analysis is sound and innovative, and represents true progress in the field of atmospheric chemistry, and should be published.

Major comments: While I believe that the work described in this manuscript is novel and important, the novelty lies more in the interpretation and investigation of chemical composition, rather than on the development of a new methodology. I interpret the scope of AMT to be "discussion of new atmospheric measurement techniques", including new instrumentation, new data analysis methods for in situ and remote sensing measurements, and I do not see these themes very strongly in this paper. This work focuses on applying methodologies previously developed, such as vapor pressure calculations, acetate CIMS, Van Krevelen diagrams, oxidation state vs. number of carbon plots. This work can perhaps be a better fit with AMT if it focuses more on characterizing the instrument. My major comments are therefore my suggestions on how this work may be a better fit for AMT.

1. The authors stated that exact quantification of the many organic acids is important, but requires a large number of standards. Chemical ionization relies on an ion-neutral chemical reaction to create the quasimolecular ion. The sensitivity is therefore a strong function of both the kinetics (rate constant) and the thermodynamics (free energy), which can vary greatly depending on molecular structure and functional group. Are there theoretical calculations that can be performed to provide some insights? The proton transfer reaction mass spectrometer (PTR-MS) is a very similar instrument, and in many cases, the sensitivity of unknown compounds can be calculated using the ion-molecule reaction rate. Is there literature on rate constants of proton abstraction by acetate ions? Currently formic acid is the only standard (measured by a different gas monitor), but many more are commercially available and can potentially be used for understanding the range of sensitivities. One should also mention that a conve-

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nient feature of this system is that only acids are involved, which reduces the variability in functional groups somewhat. It would be important to demonstrate that the range in calibration factors for a number of acids involved in atmospheric oxidation. The manuscript would be more convincing if one quantifies the range rather than just accepting that there is a range. The ability of this instrument to quantitatively measure a large number of oxygenated compounds will be a key success of this work.

2. The instrument comparison with the Aerodyne AMS, described in Section 3.4.2, is an important discussion to better understand and interpret the measurements. Incorporating a gas/particle inlet such as the MOVI would certainly be useful, but that may be beyond the scope of this work. At the very least, more comparisons with Yatavelli et al. (2013) would be useful.

3. In the conclusions, the authors mention many new ideas for better characterizing ionization chemistry in the instrument. Some of these can be implemented quite easily. For example it should be rather straightforward to use isotopically labeled acetic acid, which s commercially available and reasonably priced. It can be used offline to measure the extent of clustering when the ratio of m/z 59 to m/z 119 is 5:1.

4. Both the title and the abstract should be rewritten to focus on the methodology. Currently, both are written in such a way that the new discoveries in gas phase composition of a-pinene and naphthalene oxidation products are the main contributions of the main contributions. Specifically, the first sentence after the overall introduction in the abstract is, “Here we examine gas-phase O3 and OH oxidation products of a-pinene and naphthalene formed in the PAM flow reactor. . .”. Immediately after that, the authors report the OH oxidation exposures used and the consistencies with previous experiments. It would seem to me that focusing on the methodology to analyze soft ionization data would make a better manuscript for AMT, and a-pinene and naphthalene are used only as examples.

It seems to me that an AMT paper would be focused on exploring these ideas, while

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the current manuscript should be submitted to journals like Atmospheric Chemistry and Physics, Atmospheric Environment, Environmental Science and Technology, or other atmospheric chemistry journals. Again, I defer the decision about the scope of this paper to the editor.

Other comments:

- The nC distribution in Fig. 4 is very interesting. One can observe the reaction chemistry though the nC distribution: naphthalene dissociates into mostly even carbon number products because of its molecular structure. Why would there be strong signals of C9 and C7 compounds? Acetate clustering does not explain these compounds, because it is a C2. Is it possible for larger compounds to dissociate in the ionization and mobility region (e.g. loss of CO2 or formaldehyde)?

- In both the abstract and the conclusions, the authors suggest that the method can be applied to other reagent ion chemistries. The authors should also mention that other reagent ion chemistries are potentially more useful and easier to analyze since some do not contain carbon atoms (such as iodide).

- Page 6392 Line 1: The tubing was heated to 200C. Are there any concerns of decomposition of acids?

Technical comments:

- Page 6391 line 9: Presumably the authors mean a-pinene ozonolysis instead of isoprene

- Page 6391 Line 12: It is unclear if the achieved resolution of 4000 is for the V- or W-mode.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 6385, 2014.