

Interactive comment on “A switchable reagent ion high resolution time-of-flight chemical ionization mass spectrometer for real-time measurement of gas phase oxidized species: characterization from the 2013 Southern Oxidant and Aerosol Study” by P. Brophy and D. K. Farmer

Anonymous Referee #1

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This manuscript describes and characterizes the Aerodyne High Resolution Time of Flight Chemical Ionization Mass Spectrometer (HR-TOF-CIMS) operated as a switchable reagent ion (SRI) HR-TOF-CIMS, as well as data from this instrument collected during the Southern Oxidant and Aerosol Study (SOAS). The reagent ion chemistry was switched frequently between iodide and acetate ionization. Background determinations and formic acid calibrations were conducted hourly, and this was found neces-

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sary for tracking instrument performance and quantifying formic acid.

The Aerodyne HR-TOF-CIMS is a powerful and still relatively new instrument undergoing significant development in data analysis and interpretation. By switching the reagent ions a larger number of species can be analyzed using the same mass spectrometer. The content of this manuscript is therefore of interest to the AMT community. The manuscript is well written, and I recommend publication of the manuscript after my comments below have been addressed.

Substantial comments

Figure 9 (time series plots and associated discussion)

As part of this work the authors carefully analyze the change in instrument sensitivity to formic acid. Here they compare the (calibrated, I think) concentrations of formic acid to (uncalibrated) signals of other ions and report correlation coefficients with formic acid. Would the instrument sensitivity to these other acids be expected to change similarly as the sensitivity to formic acid? If that is the case would that not affect the correlation coefficient, and is it surprising that the correlation coefficients are this high? What would be the correlation coefficient if the concentrations of the other acids are adjusted by the observed percent change in sensitivity to formic acid?

Section 4.3 (mass defect plots)

At the beginning of the section the authors present the mass defect plots as one way to “examine complex, high resolution time-of-flight mass spectral data” and at the end of the section state that “additional dimensions of data can aid in the interpretation of these enhancement mass defect plots”

It would be useful if the authors could describe what these plots show for this particular data set and how the data could be interpreted (rather than just state that the plots could be used to interpret the data). I understand that the focus of this paper is on techniques, but at the moment the purpose of the technique (e.g. plotting the data in

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this way) is unclear to me. Also, what is the purpose of focusing on species which change by more than 5% from morning to evening? This seems to imply that species which do not change much over the course of the day are not interesting, which is not necessarily the case.

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The authors state that “while not the focus of this study, detection of acetic acid and hydroiodic acid using iodide CIMS and acetate CIMS, respectively, in a reagent switching setup may suffer a larger cross talk problem because the detected species are the reagent ions in the complementary mode. The use of hourly zeros, or zeros immediately after switching reagents, may counteract these effects but would require investigation.”

The issue of cross talk in this set-up (esp. for acetic acid and hydroiodic acid) is of interest to the research community, and I would suggest/request that the authors investigate and analyze this issue and present it in a revised version of the manuscript, esp. considering that they have the data to investigate this.

Section 5.2

The authors mention twice in this section that changes in instrument sensitivity could be associated with variability of environmental factors such as the trailer temperature. Considering this it seems appropriate for the authors to present and discuss correlations of trailer temperature with e.g. the sensitivity to formic acid.

Editorial comments

Page 3201, lines 10-15: Please reword / rewrite this sentence. It is unclear as written.

Page 3222: The last sentence of section 5.5 (reference to Aljawhary et al.) should be moved to section 4 (and removed from the discussion)

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3199, 2015.

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