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Atmospheric Measurement Techniques
Discussions

Interactive comment on “Multi-scheme chemical ionization inlet (MION) for fast switching of reagent ion chemistry in atmospheric pressure chemical ionization mass spectrometry (CIMS) applications” *by* Matti P. Rissanen et al.

Anonymous Referee #1

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This manuscript presents a system for switching reagent ions in a chemical ionization mass spectrometer, with application in the field of atmospheric chemistry. The authors discuss the use of the system with bromide and nitrate ions to investigate gas-phase oxidation chemistry. The authors present interesting data on bromide ionization chemistry, particularly the use for measuring sulfuric acid. The authors contrast their new ion source to the literature. Overall, this paper will be a useful contribution to the literature and is appropriate for this journal. However, there are a few specific experiments or pieces of information missing that are essential for proving that the multi-reagent ion

switching system works. I recommend several major revisions.

Major comments. 1.My biggest concern with this ion setup with atmospheric pressure is the potential for secondary chemistry and (unexpected) cluster formation. Along with that is a concern about titration of reagent ions when looking at complex, high concentration mixtures. These are challenges that must be addressed for publication. The key question is: in the mass spectra shown in Figure 4, how do you know that these peaks are the result of only ion + analyte adduct formation, and not multi-component clusters (i.e. formation of dimers in the reaction chamber as a result of sequential collisions)? If you apply different field strengths to the resulting ions, you will see the adducts fall apart, and be able to gain some insight into the mechanisms (see work by Lopez-Hilfiker on iodide CIMS or Brophy on acetate CIMS). The authors refer to formation of monomers vs dimers - but do not investigate whether these products are real, or the result of ion-molecule reactions in the instrument itself. The potential false production of dimers in the atmospheric pressure source seems challenging. Further, the number of ion-molecule collisions that will occur in the MION (i.e. calculate the mean free path and compare to the size of the ion source) suggests that secondary ionization and titration of reagent ions will be a challenge. The authors can demonstrate that titration of reagent ions isn’t a problem by showing the time series of the reagent ion and total ion count during an experiment in which zero air flows into the instrument and then is rapidly switched to a complex mixture from a flow reactor. If the reagent ion signal decreases, then there is evidence of titration. This doesn’t necessarily mean that the MION isn’t useful, but it is important to show the limitations of the system.

2. The two reagent ion sources clearly have different reaction times based on the diagram in Figure 1, so what is the implication of these difference? The authors need to discuss how different sensitivities or mass spectra are if they run the same reagent through the two reagent ion sources and switch between them on a constant flow of a complex mixture (e.g. output from a flow reactor). How similar (or different) are the resulting spectra and sensitivities? Figure 2 shows that there is some sort of carryover:

the nitrate signal is larger during bromide ionization than it is when neither ion source is active.

Other Comments

1. Line 242. This paragraph makes no sense: the authors claim that nitrate and bromide ionization have similar adduct binding strengths, and this somehow means that the two ionization techniques can be used. Why is this the case? Why can't quite different reagent ions be used in the system? Later in the paragraph, the authors seem to say that one can use reagent ions with different ionization mechanisms, so the authors need to clarify their point.

2. The authors use calibrations of nitrate and bromide CIMS for sulfuric acid to prove that their instrument is capable of measuring this species. However, it is not clear if these experiments were done in the 'rapid switching' mode that is the core of the paper. In fact, the inset in Figure 3 suggests that the calibration was done independently for the two reagent ions. If this is the case, then this section does not support the central claim and focus of the manuscript that the switching reagent ion system provides quantitative measurements of sticky compounds like H2SO4! The measurements must be done in switching reagent mode. Please show the timeseries along with the calibration curves (i.e. I like the setup of Figure 3 - it just needs to demonstrate that these curves hold under the actual reagent ion switching setup, and at different relative humidities).

3. Sulfuric acid detection by bromide reagent ions is a constructive direction - but needs more analysis to support the claims. Specifically, I would like to see: is there a dependence on relative humidity? And two what extent does the system form clusters vs bare ions?

4. Figure 4: I think the authors intend to show that peaks in the spectra are oxygenated organics as demonstrated by labels of O5 / O6 / O7 / etc. Are these peaks actually CxHyOz=5,6,7 or are they truly O5- ions? Please label according to actual chemical formulae.

5. I am confused by the details in Section 2.1. The authors refer to ion accelerator arrays and an ion deflector voltage. Where are these? It would be helpful to add these to the Figure 1 schematic.

6. From the schematic and description in Schematic 1, it sounds like the reagent flow is constant through both ion sources – what switches are the electric fields that ionize the reagent ions. This is an elegant solution to rapidly switching reagent ion flows. However, it does raise the question of the extent to which the (unionized) reagent flow impacts the ion-molecule reactions and chemistry in the CIMS inlet. Is there an interference from the (unionized) reagent in the mass spectra? For example, if you using a bromine precursor as a reagent flow in the first ion source, but are under nitrate ionization, do the nitrate reagent ions react with the brominated compounds? I imagine there are some combinations of reagent ion precursors where this could be an issue. The authors should (quantitatively) comment on the potential of one (unionized) reagent precursor to titrate the (ionized) reagent ion or compete with the intended reagent ion + analyte molecule reactions. 7. Line 305. The authors suggest that operating CIMS at low pressures inherently reduces signal by dilution. This makes no sense to me – in fact, operating ion-molecule reaction chambers at reduced pressure can present the advantage of avoiding titration of the reagent ion and minimizing secondary ionization reactions. The authors will need to explain their point in detail.

Technical comments

1. line 82, the authors claim that the work 'represents a significant leap in the CIMS methodology'. I disagree with the term significant 'a significant leap' and suggest it be replaced with 'progress'. This work represents progress – but 'significant leap' is an over-statement.

2. The authors note on line 96 that this is the first time in which the reagent ion scheme can be switched 'quantitatively'. This makes no sense: the reagent ion systems of the previous citations are all quantitive, but I do not understand what is 'quantitative' about

the reagent ion switching itself. Please remove the sentence or explain what you mean by this. Line 159 again refers to a ‘quantitative ion mode switch’, which just doesn’t make sense (the switch can’t be quantitative)?

3. Use of italics to emphasize points is inappropriate in research articles and should be reserved for variables or Latin terms (e.g. ‘vice versa’ or ‘in situ’)

4. Figure 5 should be labeled with what is going on (the text says that the O3 is switching – please indicate the levels so the measurements could be taken in context

5. Line 101 should read “A schematic”

6. Figure 2 caption is inadequate to understand the figure. I think that the colored traces represent mass spectral signals for the Br- ion or NO3- ion? (high resolution or nominal mass?) And then the terms at the top of the figure are the reagent ion mode that is activated? But what is the inflow air comprised of? Room air? Standards? Chamber air?

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