

Interactive comment on “A laboratory flow reactor with gas particle separation and on-line MS/MS for product identification in atmospherically important reactions” by J. F. Bennett et al.

J. F. Bennett et al.

hastie@yorku.ca

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Response to Referees

Common threads amongst the reviews:

All three referees suggested that the paper needed to expand on the advantages and limitations of the instrumentation and that this should be remedied by expanding the introduction and conclusions. While each referee had different specifics, we have expanded the introduction and conclusions to address these widespread comments.

In particular in the introduction we have clarified the ionization methods and included a

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notable omission suggested by referee #3 and highlighted the results of previous APCI work as suggested by referee #2

In the conclusion we have provided both a description of the system and its strengths. The results on the test reaction show the system is useful in a number of situations: identifying a highly volatile species in both the gas and particle phases; identification of two structural isomers and the absence (with the normal caveats of sensitivity) of an isobaric third in the particle phase; and the presence of a product only in the particle phase.

With the system description and the presented results the reader can compare the usefulness of our approach to other product studies.

Specific to Referee #1

We understand the referee's position and it is difficult to address the nagging concerns. In many ways the real value of this system will be assessed several PhDs down the road. We would, however, contend that tandem MS is still highly relevant even with the emergence of the ToF detectors. While the high mass accuracy of the ToF instruments can give the molecular formula, the tandem mass spectrometers are able to give structural information. As an example, a ToF would show an m/z 137 to be $C_8H_8O_2.H^+$ but the fragmentation of this ion in a tandem mass spectrometer could tell if it was protonated 4-hydroxy-3-methylbenzaldehyde or its isomer *m*-toluic acid by the differences in the m/z 18 and 28 losses.

Regarding the denuder, we have had a horrible time with XAD resin denuders, particularly with them becoming saturated and them becoming almost impossible to regenerate. The membrane denuder is infinitely preferable. We have put this anecdotal information into the manuscript on page 1364.

Specific to Referee #2

1. As part of the changes to the introduction, the section identified by the referee has

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been expanded. The work of Hoffmann's group has been expanded slightly, with a recently released paper cited and some specific identifications included. We have also updated the PTRMS references to the most recent description of the PTRMS-ToF

2. The estimate of loss in the denuder was to indicate that the expected amount of evaporation is relatively small. The calculation assumed a pure compound with a specific molar mass and vapour pressure. The particles are expected to be a mixture of compounds and the molar masses and vapour pressures are not well enough known yet to provide correction factors for the denuder.

3. The residence time of particles in the denuder under the optimum conditions is 90 sec. This value has been added to page 1363 of the manuscript.

4. We ran detailed experiments from 50-150°C, and found the mass spectra show very little change. Because we had concerns about the potential pyrolysis of products we chose to run these preliminary experiments at 100°C. This note has been added on page 1365 of the manuscript.

5. The reviewer has misassigned the peak. It is m/z 99, the unfragmented precursor ion.

6. The conclusion has been rewritten as outlined in the general comments above.

Minor comments

1. The IUPAC spelling of sulfate and sulfur has been confirmed in 4 places.

2. The referee is correct, IUPAC prefers L for litre so we have changed to L throughout (many places!)

3. Corrections to ppbv and ppmv are done in 4 places. We have not changed the ppb in a published title.

4. The referees suggested reference is more appropriate and has been included.

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5. This has been corrected to “widely applied method”. It is not just for particles.
6. The paragraph on pg 1359 has been rewritten to clarify that n is the number of particles.
7. The molar masses should really be mass numbers (A). To avoid confusion the molar masses have been removed and the discussion centered on m/z.
8. We all buy $\frac{1}{4}$ inch tubing, hence the use of “nominal”. The referee is right and we should use metric and nothing is really lost with 0.635 cm.
9. Good catch, thanks to the referee.
10. As with 7 above.
11. Done.
12. Done.
13. Good catch, thanks to the referee.
14. Thanks to the referee: the gas samples were run at room temperature. We have fixed the caption.

Specific to Referee #3

1. The introduction has been strengthened as described above.
2. It is unfortunate that the comment is truncated; however the referees point is clear. They implicitly raise the question of the relevance of the reaction conditions used when they are different from that in the atmosphere. This is foremost in our minds. The purpose of this equipment is to allow us to make more extensive measurements of reactions to examine exactly that. The data shown here are intended to show the utility of the tool in studying reactions. Product studies such as those we have initiated will contribute to our understanding of the impact of reaction conditions on the products.
3. The referee has used the residence time in the reactor for this calculation not the

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residence time in the denuder. This is 90 s and has been included in the manuscript on page 1363.

4. Because of the inability to protonate, the detection limit for m-xylene is terrible, it is about 10 ppmv barely enough to see it reacting. For the particles we sample about 1×10^8 particles for a 250 ms scan. These numbers are included in the manuscript.

5. The referee is right. To our knowledge there is no evidence for the production of M+ via that mechanism in an APCI source. We have changed the wording to remove the erroneous mechanism..

6. We were not clear enough on this point. We said the 35 nm particles were smaller than those generated by reaction. The referee rightly points out that at very short times the particles are smaller. What we think is relevant is the size of the particles as they leave the reactor. We measured the size distribution of the organics as they left the reactor. These have a geometric mean and std deviation of 128 nm and 1.66. Thus the test particles are indeed smaller at the 2 sigma level. We have clarified the sentence on line 5 on pg 1364.

7. Same as for reviewer 2. We ran detailed experiments from 50-150°C, and found the mass spectra show very little change. Because we had concerns about the potential pyrolysis of products we chose to run these preliminary experiments at 100°C. This note has been added on page 1365 of the manuscript.

8. We have been reluctant to make tables of the 39 spectra as we thought they would add little to the discussion. We will work with the editorial staff to ensure the eps files are sufficiently clear. In the text we have clarified that Fig 6c is the unreacted mixture and that the peaks observed are primarily those due to IPN, its contaminants and their dimers and water clusters. The referee is correct in observing the m-xylene peaks are small, as are all aromatic hydrocarbon peaks. This too has been clarified on page 1365. The H₂O was not varied in this work. The H₃O⁺ and H₃O⁺.H₂O ion concentrations were not depleted so there was always sufficient ionization for product identification.

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9. We used authentic samples to assign the peaks for the dimethylphenols. There was evidence of overlapping reaction products from the reactor at m/z 123. Hence we used m/z 122 as that is a cleaner tracer for dimethylphenol. This has been clarified on pg 1365.

10. The suggestion is a good one, however with the sensitivity available we cannot decrease the reaction time sufficiently to allow this analysis. Connecting the denuder and mass spectrometer to a more slowly reacting system, such as a chamber would generate complementary data. Gas particle partitioning remains the holy grail but at this time the evaporation in the denuder is probably the biggest hurdle in making the particle measurements quantitative

11. As above the conclusion has been expanded. The other points have been addressed in 2 above.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 1351, 2009.

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