

## **General Overview:**

The manuscript, "The ion trap aerosol mass spectrometer: improved design, first field deployment, and the capability of differentiating organic compound classes via MS-MS" by Fachinger et al. provides a useful next step in describing a tandem mass spectrometer (IT-AMS) for analysis of organic aerosols. The portions of the manuscript dealing with MS<sup>n</sup> capabilities and the field deployment are of particular interest and offer the reader new information. However, the parts of this manuscript outlining improvements to the instrument first presented by Kürten et al. IJMS 2007, and alluded to in Fachinger (Mainz thesis 2012) do not seem to be significant advances to the instrument or its capabilities to warrant publication in their own right in their current state and should play a more diminished role than suggested by the title of the article. Furthermore, as the Fachinger thesis is published in German it is not accessible to the non-German speaking audience of AMT, and asking the audience to refer to this paper to describe in detail the improvements to the instrument is unhelpful to the reader. In addition, as a thesis has not undergone outside and anonymous peer review, the statements in a thesis cannot be relied upon to the extent used in this manuscript.

The paper claims the IT-AMS is "capable" of quantitative measurements in the field but the instrument was not calibrated in the field using an external standard as to yield a series of mass concentrations over time. The capability of an instrument to be quantitative needs to be backed up with lab or field experiments where the instrument actually is calibrated and determined to be quantitative. It would have been helpful if more information on the field calibration of the IT-AMS and TOF-AMS were given.

There is enough new information in this manuscript however, to support the publication of this manuscript in AMT if the following major corrections are made. I recommend resubmitting the manuscript after concerns with calibration and references to the Fachinger 2012 thesis are addressed.

## **Review of content**

### **Major concerns:**

**"Improved Design"** – the Kürten et al 2007 paper referenced no need for an improvement in design in order to provide mass concentrations of aerosol components or to become field deployable. To state then in this manuscript that major improvements were needed to make the instrument field deployable leaves the reader questioning the validity of the claim. Of course minor improvements to instrumental design and software modifications normally occur over time but the improvements mentioned could not be published as a stand-alone paper as they do not fundamentally change how the instrument is operated, but only offer minor improvements on existing systems. In my opinion, the "improvements" to the instrument were antidotal unless a direct before after comparison of performance characteristics is given. Furthermore, the Fachinger thesis is asked to be referred to but it is not written in English in which AMT is published. This limits to usefulness of this citation in the following two ways. First a thesis has not undergone scientific peer-review beyond the student's examination committee, and secondly, it is written in German which limits its usefulness to only those AMT readers fluent in both English and

German. This major concern can be addressed in one of the following ways. 1. Omit much of the section dealing with the instrument modifications and focus on the TOF-AMS intercomparison and the MS<sup>n</sup> data, or 2. expand this section to include a more detailed explanation of the instrument not requiring as much reference to the Fachinger thesis.

**“First field deployment”** - The IT-AMS vs Q-AMS intercomparison for nitrate in Kürten et al 2007 seemed to already be the first field deployment of the IT-AMS instrument although not in its currently modified state. Furthermore, because the instrument was calibrated it was able to give a mass concentration time series, which was not done in the current manuscript. Since the IT-AMS had already been field deployed (although perhaps locally in Mainz) and intercompared to a Q-AMS, the claim here in the title that this is the first field deployment seems overstated.

**Suggestions for the title:** I suggest rewording the title and refocus the paper to focus less on improvements to the instrument and this being the “first” field deployment and more on the MS<sup>n</sup> capabilities and intercomparison with the TOF-AMS.

**Quantification and intercomparison:** Additional experiments in which the TOF-AMS and the IT-AMS are both calibrated with externally generated aerosol of known mass concentration should be presented. This type of calibration would validate the IT-AMS calibration method presented in the article as was done for nitrate in the Kürten et al. 2007 paper where both instruments were sampling the same laboratory generated aerosol sample. The IT-AMS results were thus only given in ion rate which the TOF-AMS results were given in mass concentration ( $\mu\text{g}/\text{m}^3$ ) but neither seemed to be calibrated in the field. The reader is left with the question as to why the IT-AMS not was not intercompared with the TOF-AMS in the field using laboratory generated aerosol. If an intercomparison (similar to that described in the Kürten et al 2007 paper) was conducted, it should be included in the manuscript. If the intercomparison was not done I would suggest conducting the intercomparison after the fact using the same instrument parameters as when the instruments were in the field. Not having any field or lab intercomparison so that both instruments are analyzing the same limits the usefulness of the data presented in this manuscript to other readers. For instance it is important to see if one instrument is reading a higher or lower mass concentration than the other which can offer insight into inlet effects, instrument specific contamination, or bias in one instrument over the other. Furthermore, presenting IT-AMS only in ion counts makes it difficult for others in the field to compare their data with the data in this manuscript. Without the intercomparison only the linearity ( $R^2$ ) of the IT-AMS ion rate vs. TOF-AMS mass concentration can be assessed which is done in this manuscript. But the IT-AMS limit of detection thus relies on the performance of both the IT-AMS and the TOF-AMS which limits the usefulness of this data and suggests to others that a TOF-AMS must be deployed whenever an IT-AMS is deployed in order make quantitative determinations.

## Specific comments pertaining to content:

### Page 2

#### Section 1: Introduction

In general -

- One of the benefits of ion traps is the capability of ion/molecule reactions inside the trap which can also be utilized to differentiate isobaric or isomeric ions. This concept should be mentioned as an advantage of ion traps especially since the authors mention the possibility of disadvantageous ion/molecule reactions later in the manuscript.
- The manuscript could be improved by providing references to show the usefulness of differentiating between carboxylic acids and sugars in aerosols.

Line 11: Please be more specific in what types of “mathematical algorithms” have been used.

Line 14: Not sure what “a partial loss of molecular information” is referring to specifically. Do you mean that the ionization could be so complete as to eliminate the molecular ion peak? Or do you mean that hard ionization makes the interpretation of a mixture more difficult? Of course the  $m/z$  of the fragments gives much molecular information, however I am guessing the authors probably meant that the molecular ion  $m/z$  is lost especially for higher molar mass ions.

Line 13-17 – “On the other hand” - I am not sure what information the author is trying to convey here as EI does not “reduce” complexity of the mass spectrum but increases it compared to soft ionization methods such as chemical ionization. In fact EI of mixtures creates additional complexity which is what the previous sentence addresses requiring the incorporation of mathematical algorithms.

Line 15-16 : “while some important information on the original molecular structures are still retained” - Please state what information is retained. Molecular ion  $m/z$  is retained but molecular structure is determined from the fragmentation pattern which in a mixture can be convoluted which requires the mathematical algorithms referred to previously.

Line 26: “differentiation between fragment ions of the same elemental composition, but with different structural formulas.” Is there a more concise scientific term for these types of ions such as “isomeric ions” that could be used or defined here?

### Page 3:

Paragraph 1: I am at a loss as to how a hard ionization technique such as Thermal Desorption (which causes some fragmentation) coupled to EI which is a “hard” ionization source, could provide “a strong reduction in complexity of organic aerosol mass spectra” compared to soft ionization sources. Does “With these systems” in line 8 refer to the IT-AMS or in fact are you referring to the soft ionization sources listed before the paragraph shifts to talk of the IT-AMS. Hard ionization produces more fragments and thus more complexity especially for mixtures of molecules. Soft ionization produces less fragments and thus a less complex mass spectra.

Line 10-13: The Kürten et al. 2007 paper states in its abstract that the instrument at that point was ready for field deployment. I am not convinced that field deployment was impossible without the modifications to the instrument described in this paper. This discrepancy needs to be resolved. Either the instrument was ready for field deployment in the 2007 paper or it wasn't. As the IT-MS was not calibrated in the field it still may not be considered "field deployable" until it can quantify aerosol components in units of mass concentration.

Line 16 "and potentially quantify" this term needs to be rephrased as either a technique can quantify or it can't.

## **Section 2: Instrumental development**

- It is difficult to tell whether further advances after Fachinger 2012 were made or whether the all of the advances over the Kürten et al. 2007 paper were described by the Fachinger 2012 thesis.
- Also again since Fachinger 2012 was not peer reviewed the reader should not be referred to this thesis multiple times for clarification because the thesis is not peer reviewed and it is not in English, the language of AMT.

### **Page 3**

Line 24: Since the aerodynamic lenses are referenced to Fachinger 2012, were they the same lenses used in the Kürten et al. 2007 paper? If so, please reference the Kürten paper instead of Fachinger, if not please describe the differences over the lenses in the Kürten paper.

Line 28: Describe to what extent the "flash-vaporization" also causes some ionization or fragmentation before EI causes further ionization and fragmentation.

Line 32: In reference to "high purity helium" please state the purity and vendor actually used and the vendor.

### **Page 4**

Line 1: it is stated the instrument can provide quantitative information as in Kürten et al. 2007 while the last paragraph in the introduction the instrument is only potentially quantitative.

Line 2: Define what you mean here by reproducibility of the measurements. If the measurements in Kürten et al. 2007 were not reproducible doesn't that call into question the validity of the 2007 paper? Or are you referring to lack of reproducibility as a lack precision in the measurements?

Line 5: It is stated that the instrument is now more "versatile". Wasn't the instrument always capable of the measurements made in this paper? Please explain the instrument now more versatile than it was before?

Line 8-10: "We only describe the most important changes in detail here; other modifications are only briefly summarized and their details can be found in (Fachinger, 2012)." Since Fachinger is not peer reviewed and not written in English the details mentioned have not been scientifically reviewed and are

inaccessible to all those who are not bilingual in German and English. Please either remove most of this section or provide the details here so that they can now be peer-reviewed in English.

Line 11-15: In the ion trap, instead of the ceramic washers used by Kürten et al. (2007) as spacers between the ring and end cap electrode, now ruby spheres (diameter  $6 \text{ mm} \pm 0.635 \text{ }\mu\text{m}$ ) sitting in precise countersinks ( $1.3 \text{ mm} \pm 10 \text{ }\mu\text{m}$ ) are used for a more defined mounting (insert B). This allows for a more reproducible assembly of the electrodes, and consequently more reproducible voltage settings” To state an improvement the original conditions must also be stated. Please quantify the reproducibility in assembling the electrodes before and after the improvement were made. Furthermore, ion optics are electrically isolated from each other so that the ring and endcap can voltages can be set independently, how then could imprecision in electrode spacing result in a lack of “reproducible voltage settings”. Please provide quantitative proof, or else only state the change without stating that it made an improvement.

Line 15-19: Please state quantitatively to what extent helium flow changed in the original setup over the course of several days. Again quantitative evidence is given for the updated system but not for the original system.

Line 18: State the orifice diameter of the critical orifice.

Line 19: Please state the manufacturer and flow range of the pressure-controlled mass flow controller mentioned.

line 22: The ion source need not be pulsed if a gate electrode between the ion source and trap is used. Here the ions in the source are continuously produced and the gate electrode voltage is lowered in order to fill the trap, and raised during ion manipulation and scanout to prevent additional ions from entering. Was this type of operation used and found deficient for some reason?

Line 25: Was the filament emission current monitored? If so please quantify the instability.

Line 28: Better reproducibility is mentioned? State exactly what is more reproducible and how it is measured.

Line 30-34: Again I suggest that since the specifics are mentioned in Fachinger 2012 that this section describing minor improvements either be expanded on in order to peer review these claims in English. Some of the points like improving the instrument housing, and improving the electrical and communication connections seem like more trivial modifications and can be omitted unless they can be tied back to quantitative instrument improvements.

#### **Page 5:**

Line 1: Please state the version of LabVIEW used to write the program.

Line 1-6 – again since Fachinger 2012 is referenced here the nontrivial details referred to need to be provided here.

#### **Section 3: laboratory and field measurements**

## Page 5

Line 8: please include the stated purity and manufacturer of each chemical used. This could be done in a supplemental table or added to the existing table.

Line 12: Was the ToF-AMS run in parallel with the IT-AMS so that they were both analyzing the same sample from the nebulizer? Consider making a schematic diagram of how the instruments were connected together with the nebulizer and/or with the particle counter.

Line 17: Please mention to what extent each instrument was measuring the same air mass since the measurements seemed to be taken 5 meters apart and temporally (IT-MS 30s time resolution, ToF-AMS 60s time resolution). Could some of the variability in the instruments mentioned later really be due to the instruments measuring slightly different air masses either spatially or temporally?

Line 19: How can the instruments be sampling “in parallel” if they were sampling from two separate inlets? Were the inlets to each instrument both sampling from a common manifold? Or do you just mean that each instrument was sampling at the same time but from two different (although close) locations.

Also Sobanski et al 2016 doesn't mention the ToF-AMS or the IT-AMS and only refers to instruments in a mobile laboratory (MoLa) for measuring aerosol parameters, thus the sentence should be rewritten so that Sobanski only references the field campaign and not that “continuous measurements of ambient aerosol using the IT-AMS and a high resolution ToF-AMS were continuously performed” during the campaign.

Line 27 – Kürten et al 2007 states the mass range was up to 200  $m/z$  without using the mass range extension. Did the mass range decrease over time or did the modifications stated previously lower the mass range?

Line 27-28: “ions of  $m/z$  of interest were isolated (typically within a range of  $\pm 5 m/z$ ) by broad band excitation using a filtered noise field” Figure 4 show isolation was outside of the  $\pm 5 m/z$  range and looks more like -10 to +5  $m/z$  in that particular instance. Please revise either your isolation range, or use a different mass spectrum in figure 4.

Line 31: Please state the versions of IGOR Pro and MATLAB used.

## Page 6

Line 3: Please include information on how the “background effects” were performed in the methods section including how the particle free air was generated.

Line 3: Do you have a quantitative way to state or argue that ionization efficiency in the TOF-AMS didn't change during transport of the instrument to the field location, or over the course of the campaign? Did you do any field checks of the ionization efficiency? Please add additional information on how the TOF-AMS was calibrated in Section 2.

Line 4-5: Again it is vague which “co-located measurements” were taken and how “good agreement” was determined since Fachinger 2012 is not peer reviewed. Please expand this section.

Line 5-10: Please explain more fully (or give a reference to) how detector intensity (in units of voltage or current) is used to calculate an ion rate in units of Hz.

Line 16: averaging only minimizes the statistical uncertainty if the relative instrumental drift between the two instruments is negligible compared to the variation in the measurements. What evidence does the authors have in order to quantify instrument drift? It is stated that 1h average mass spectra “typically” have the same features, but do the atypical results skew the 11day average?

Line 18: Could the difference in the instrumental response below  $m/z$  30 be due to the gating of the electrons in the IE region of the IT-AMS or different voltage settings between either the IE region and the ion trap or ToF region? Furthermore could the difference be due to decreased trapping efficiency of low  $m/z$  ions.

Line 23: Please quantify “much smaller”

Line 28 Define what it means that “this plateau disappears”. For example, in the plateau disappears then does it then increase like the IT-AMS data?

## Page 6

Line 3: Where these calibrations done and accounted for?

Line 4: The term “is comparable” should be quantified.

Line 6: “is transferable” : the measurements may be transferrable but since there is still a large variation in the data, transferring the data would cause large uncertainties in the IT-AMS results, and would require that a ToF-AMS always be co-located with a IT-AMS. This requirement is a major deficiency of the IT-AMS for field campaigns and should be addressed in the manuscript.

Line 9: is “ $m/z$  48 to 64” supposed to read, “ $m/z$  48 and 64” since only  $m/z$  48 and 64 are designated at sulphates in the upper part of figure 2?

Line 15-16: “No calibration measurements were performed for the IT-AMS.” This is a major deficiency of the manuscript as this means the IT-AMS mass concentrations must be tied to the ToF-AMS which was also not calibrated in the field. The authors must explain why neither instrument was not calibrated in the field and intercompared using the same aerosol generation source.

Line 20: Please comment on the fact that the 1h  $R^2$  values for nitrate are lower than that of the 10min data.

Line 24: It should be noted in the manuscript that Drewnick et al. 2009 were calculating the detection limits for a TOF-AMS and not a IT-MS

Line 25-30: Using the “linear” relationships in figure 3 to calculate mass concentrations for the IT-AMS will produce large uncertainties in the limit of detection for the IT-AMS (especially for sulphate). The uncertainty in the detection limits must be calculated and reported. Also if the  $R^2$  value for the 1h measurements of nitrate are larger than the 10min data, how can the limit of detection for the 1hr data be lower than the 10 minute data for nitrate. Furthermore, if it was claimed in the previous paragraph that the IT-AMS signal for sulfate is lower than that of nitrate, and that sulfate has a lower signal to noise ratio compared to nitrate, how can sulphate and nitrate have the same detection limit? This discrepancy needs to be explained in the manuscript.

## **Section 4.2 and following**

These sections are the highlight of the paper in my opinion and quite well reasoned.

### **Section 4.3.2**

The authors make a convincing argument that  $MS^2$  studies can differentiate sugars and carboxylic acids for fragment ion isomers. However, it seems more straight forward to differentiate these species based on their molecular ions in the  $MS^1$  spectrum as all of the species in table 1 have different molar masses. The manuscript could be also be improved by differentiating molecular ion isomers by looking for unique fragments of each isomer, or differences in the ratio of fragments for isomers that do not have unique fragments.

## **Section 5**

### **Page 12**

line 11-12: It is stated that that the detection limit “were found to be sufficiently low to allow for  $MS^2$  studies on atmospheric particles under favorable ambient conditions (0.6 micrograms/ $m^3$ )”. The 0.6 figure seems to come not from either ambient measurements or from  $MS^2$  measurements. The 0.6 figure seems to come from the  $MS^1$  measurement of tryptophan under laboratory conditions. I would suggest either referring to the limits of detection for organics, nitrates, and/or sulphates from the field campaign, or the  $MS^2$  detection limits from the tryptophan measurements which were stated as being 7 micrograms/ $m^3$

**Figure 1:** Please add the pressure into the ion trap region, and show in which sections turbopumps or other pumps are located. In subpart “A” show that He comes from a compressed gas cylinder and what the flow rate of He is into the ion trap. For “B” it looks like these figures are taken directly from Fachinger 2012 and should be referenced as such.

**Figure 2:** Please make it clear in the text or caption how the relative signal was calculated. Are these ratios of raw detector output or ratios of ion rates? Also it is confusing after reading the caption if the top graph is calculated from the relative signals from the bottom graph. If this is so then the bottom and top graphs should be switched. I suggest changing the bottom graph’s y-axis label to “signals relative to  $m/z$  28. Also from the caption it is unclear as to how the normalization occurred. Was the IT-MS data normalized to the  $m/z$  28 value from the IT-AMS, and the ToF-AMS data normalized to the  $m/z$  28 from



the ToF-AMS, or was data from both the IT-AMS, and ToF-AMS normalized to the IT-AMS m/z 28 signal. Also there seems to be some data that is missing such as m/z 13 and 15 that show up in the bottom graph. Below m/z 20 some of the ToF-AMS data is larger than the IT-AMS which obscures the IT-AMS data completely. M/z 21 for the ToF-AMS is not existent in the bottom graph the m/z 21 is shown the top graph. M/z 88 shows a very small signal for the ToF-AMS compared to the IT-AMS signal, but in the top graph m/z 88 has a similar relative signal to m/z 87, and 89. Unless I am reading the graph incorrectly, I am not sure how this discrepancy could occur. Finally, since data below m/z 30 is not useful in differentiating organics, sulphates, or nitrates you may consider omitting this data and only briefly referring to it in the text of the manuscript.

**Figure 3:** For the sulphate graph please align the 0 measurement for the IT-AMS with the 0 measurement of the ToF-AMS like it is for the nitrate and organics graphs. It seems as though some of the data for the IT-AMS might give negative ion rates and thus under the detection limit for the instrument. Please also include a horizontal dotted line on the IT-AMS graph indicating the calculated limit of detection of the instrument. It looks like the data for nitrates after September 8<sup>th</sup> might also be below the detection limit, so this should be discussed in the text. Finally, local date and time, should be designated in the caption vs UTC so that the reader knows the time zone and if local time includes daylight savings time.

**Figure 4.** The vertical dotted line in graph a) should be defined in the caption. It looks like the dotted line is used to differentiate a region to the left which uses the left y-axis, and a region to the right that uses a different y-axis. Please include only a graph of the isolation step before graph b).

#### **Specific comments pertaining to format:**

#### **Page 2**

Line 7: "The currently most widely..." suggested rephrase to "Currently, the most widely"

line 10: delete "here" and change "is" to "are" in the sentence "Since here a large number of different molecules is analysed simultaneously"

Line 13: Suggest changing "strongly fragmented" to "highly fragmented"

Line 18: "high resolution" to "higher resolution" as high resolution mass spectrometry often refers to Penning trap instruments such as ICR or Orbitrap which have resolutions orders of magnitude greater than TOF. It would also be good to state here what the resolution of IT-AMS is from the Kürten et al. 2007 paper.

Line 25: consider removing "some" in "While some information on elemental composition".

#### **Page 6**

line 15: Please rephrase this sentence so that it doesn't end in "with."

## **Page 12**

line 5: remove the word "regular" in "regular ToF-AMS"

page 12 line 30: replace "on" with "in"

## **References**

Fachinger, J. R. W.: Das Aerosol-Ionenfallen-Massenspektrometer (AIMS): Aufbau, Charakterisierung und Feldeinsatz, PhD thesis, Johannes Gutenberg University Mainz, Mainz, 2012.

Kürten, A., Curtius, J., Helleis, F., Lovejoy, E. R., and Borrmann, S.: Development and characterization of an ion trap mass spectrometer for the on-line chemical analysis of atmospheric aerosol particles, *International Journal of Mass Spectrometry*, 265, 30-39, 2007.

Sobanski, N., Tang, M. J., Thieser, J., Schuster, G., Pöhler, D., Fischer, H., Song, W., Sauvage, C., Williams, J., Fachinger, J., Berkes, F., Hoor, P., Platt, U., Lelieveld, J., and Crowley, J. N.: Chemical and meteorological influences on the lifetime of NO<sub>3</sub> at a semi-rural mountain site during PARADE, *Atmos. Chem. Phys.*, 16, 4867-4883, 2016.