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Atmospheric Measurement Techniques Discussions

Interactive comment on "Peak fitting and integration uncertainties for the Aerodyne Aerosol Mass Spectrometer" *by* J. C. Corbin et al.

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1 General Response (copied to both reviewers)

We consider ourselves fortunate to have received two detailed and careful reviews for our manuscript "Peak fitting and integration uncertainties for the Aerodyne Aerosol Mass Spectrometer". The review of Referee #1 was thorough and detailed and addressed exactly the issues that our manuscript attempted to focus on, highlighting what we can agree were the most meaningful areas for significant improvement. The review of Referee #2 addressed important issues that we did not intend to address, such as the relevance of peak-integration uncertainties to general AMS data products, and thus

also led to significant improvements in our opinion. These reviews as well as the comment by M. J. Cubison have spurred a number of changes in the manuscript, which we begin by describing generally in this section.

The most significant changes have been to the section on multiple overlapping peaks. The section has been rethought and rewritten. To justify these changes, two new figures have been inserted in the isolated-peaks section, to illustrate the importance of m/z calibration biases to m/z calibration imprecision and thus peak-fitting imprecision. One figure compares peak-fitting imprecisions estimated via slightly different approaches, and also serves the purpose of responding to some of the reviewers' comments. The other figure plots m/z calibration biases and imprecisions against peak-fitting imprecisions, providing a general reference which would be valid for any instrument. Thus both figures simultaneously address specific referee comments as noted in the detailed response.

The second of the new plots provides a basis from which the Monte Carlo uncertainty estimation described in the manuscript can be extended to any set of overlapping peaks. The only requirement is a conservative estimate of the m/z-calibration precision, where conservative is defined as being significantly greater than the m/z-calibration bias (mass inaccuracy). The latter can be estimated directly from a mass spectrum containing peaks of known composition.

In addition, the comment by M. J. Cubison has led us to avoid reproducing the figures that were similar to those presented in Cubison and Jimenez (AMT 2015). Rather, we have shifted the focus of our manuscript more heavily towards the estimation of multiple-overlapping-peak imprecisions, which was outside the scope of Cubison and Jimenez's work. A number of minor changes to the text result from this, for the sake of flow, which are not detailed here but highlighted in the attached revised version.

Detailed responses to the remaining referee comments follow. Figure numbers refer to the AMTD figure numbers, unless specified as new figures by "new Fig. x".

2 Detailed Responses to Referee #2

Referee #2's major comments were about the scope of the discussion with regard to the implications of our results. Excluding the summary of our manuscript, his/her major comments were:

> *"An important finding presented in this manuscript is the fact that – contrary to Poisson-counting related uncertainties – the relative uncertainty due to analysis effects does not decrease with increasing peak intensity. This results in significant uncertainties also for large peaks, contrary to the general approach used in the analysis. Especially in statistical approaches like PMF where the uncertainty of the individual peaks plays an important role for the further analysis, this could result in bias of the results of such analysis steps. Generally, the manuscript is well and clearly written with few typos or inconsistencies. The subject of the manuscript is definitely suited for AMT. The analysis performed and presented in this manuscript was thoroughly performed and the results seem to be reliable. Nevertheless, after reading through the manuscript I was rather disappointed: In relation to the useable information the reader obtains, the manuscript is rather long. All the analysis steps and approaches are very detailed described and discussed. After struggling through the whole manuscript the reader is left with the information that for this single data set obtained with this single instrument a 4% uncertainty due to peak position and a 2.5% uncertainty due to peak width is introduced by the analysis, but these values might differ for different data sets with the same instruments, they likely differ for different instruments and they definitely differ for all the peaks which are not isolated peaks – and there is no clear information what to expect under all these conditions. With the title "Peak fitting and integration uncertainties for the Aerodyne Aerosol*

> *Mass Spectrometer" I would expect some information about what level of uncertainty due to analysis steps to expect for my instrument and my data set. In addition to information on individual peak uncertainty I would expect information on overall mass concentration or PMF result uncertainty due to the analysis. Instead I learn about a method to analyze these uncertainties and I learn that these uncertainties might be very different for different instruments and depend on various influences which are not known well enough. At the end this is not a paper on "peak fitting uncertainties" but a paper describing "a method to evaluate peak fitting uncertainties". Taking into account that the uncertainties presented in this manuscript are in the order of <5% and the additional uncertainties for non-isolated peaks cannot be generally specified and could be somewhere between 0 and 100% I wonder whether reading and understanding all these details is it really worth the effort for me when I don't learn much about the uncertainties I have to expect in my own data set. Therefore I suggest that before publication the manuscript is extended to provide more generally useable information for the general AMS user. For this purpose a discussion of how the differences between different instruments, tunings and mass resolutions affect the analysis-related uncertainties and how these uncertainties translate into uncertainties of final "products" like mass concentrations of individual species would be helpful. Also a discussion of how large typical uncertainties due to non-isolated peaks are under typical measurement conditions (for different kinds of instruments) and how this will affect the uncertainty of the final products. Finally a discussion of the uncertainty introduced into PMF results as a consequence of wrongly defined uncertainties of the large signals would be very interesting to the AMS user. As mentioned before, this manuscript reflects thorough work, well presented. My major concern is its usefulness to the potential readers which I see very limited at the moment since all the results are clearly stated not to be generally valid.*

> *Generally, this investigation and discussion is very relevant for the AMS community. Therefore I strongly support publication of this manuscript after it was extended to provide more directly useable information to the reader. Further general and detailed comments which also should be considered before publication are listed below."*

In response to these comments and those of Referee #1, we have significantly revised the manuscript. The revisions include, in particular, a discussion of how peak-fitting uncertainties translate into final products (only when significantly influencing PMF results do they do this) in the introduction and PMF subsection of Section 6. The revisions also include a much greater emphasis on overlapping-peak uncertainties, which are much larger than isolated-peak uncertainties. Moreover, the new Fig. 10 presents a graphical map of peak-fitting imprecisions which is general to any mass spectrometer. The new Fig. 10 also implies that the Monte-Carlo approach described in the manuscript can be applied to any combination of peaks, because when m/z-calibration imprecision is simulated as significantly higher than m/z-calibration bias, the importance of the bias becomes negligible. These major changes address Referee #2's comments by extending the validity of the results significantly, although we would like to note that only the specific value of the μ-prediction imprecisions and biases and of the relative imprecision term were specific to our instrument in the AMTD version of the manuscript.

We are grateful to Referee #2 for spurring on the enhanced generality of these results and we respond in more detail to some of his or her comments below.

3 Specific Responses to General Comments by Referee #2

1. "The title seems rather too general for the content of the paper which is several times claimed not to be valid for other instruments."

Here we must disagree. In the submitted manuscript, only the specific values given for the various imprecisions were not valid for other instruments, the general trends are valid in general and were stated as such. In any case, the implications in the revised manuscript are much broader.

The first part of the title, "Peak-fitting and integration uncertainties" is quite specific in referring to the topic of the manuscript. Since the manuscript has explicitly considered the peak-fitting and integration techniques used "for the Aerodyne Aerosol Mass Spectrometer", this is the second part of the title. We have added an additional phrase to the title, "effects of mass accuracy on location-constrained fits", to better highlight the aspect of this topic on which conclusions were drawn. These conclusions, and the accompanying computer code, are general for any analysis procedure applying location- and width-constrained fits to pseudo-Gaussian peaks.

2. "It would be interesting to find information on the overall uncertainty of the final "products" of the AMS like total species, elemental ratios or PMF factor results."

This was certainly something that should be explained in the manuscript. For the first two items in this list (the mass concentration of chemical species and elemental ratios), this information would seem a natural progression from our analysis, but is actually not relevant. The introduction now contains the following paragraph:

Here, "uncertainty" refers only to the internal imprecision of the AMS, defined below, and not to the overall accuracy of AMS-based mass concentrations, elemental ratios, or other data products. The calculation of both mass concentrations and elemental ratios requires additional calibration factors which dominate their overall accuracy of roughly $\pm 25\,\%$ *(Canagaratna et al., 2007; Bahreini et al., 2009; Aiken et al., 2008; Canagaratna et al., 2015). Such inaccuracies or* *imprecisions are not relevant for the statistical modelling of AMS measurements and are not influenced by the peak-integration imprecisions discussed below.*

As the last item in his/her list, the Referee requested a discussion of PMF factor uncertainties. These were already explicitly discussed in the dedicated Section 6.4, so we assume the Referee was referring to PMF-factor mass concentrations, which are now more-explicitly discussed in Section 6.4.

3. “How do the uncertainties differ for W- and V-mode measurements; how do they differ between instruments, between different tunings of one instrument which will likely change the peak shape?”

Sections 3.4 and 3.5 showed that the peak shape has a minor effect on the issues discussed in the manuscript, and that μ-prediction errors are the largest uncertainty. Also μ-prediction errors may concievably be affected by instrument tuning, but we consider this unlikely. Most significant is that W-mode measurements reduce the number of points per peak. However, this number is not constrained between instruments and we prefer not to discuss it quantitatively. In pracatice, this issue is quantitatively addressed by using the actual m/z basis of the data during the recommended method.

4. “The m/z calibration seems to be the most critical factor for the analysis uncertainty. How can this calibration be improved?”

Please refer to the third paragraph of Section 6.2 (page 3497), beginning with “an improved calibration procedure would be an obvious recommendation for reducing μ-prediction errors”.

5. “is it at the end not the error in the calibration but effects which affect the behavior of individual ions to make the respective peaks deviating from the m/z calibration (e.g. location of the ionization, thermal velocity effects, ...)?”

Please refer to the second paragraph of Section 3.3 (page 3483): “The peaks in Fig. 2 span a range of different m/z [...] and represent a range of different species. For example, C3+ ions formed when BC vaporizes at close to 4000 K, whereas C2H3O+ and C3H7+ ions formed when organic PM vaporizes below 873 K”.

6. “It would be very desirable and it would improve the usefulness of the manuscript for the general AMS user if general information (i.e. valid for all instruments and different tunings and mass resolutions) on the expected uncertainty of the analysis would be available. Since there are several dependences of these uncertainties on various parameters associated with the different instruments it might be a solution to provide graphs where uncertainty is plotted as a function of various parameters [...]”

Upon first reading, this request seems almost impossible; tuning for example is not a quantity that can be considered quantitatively. Nevertheless, we believe the new Fig. 10 addressed this response directly. The small difference between the real and idealized peaks (first and second columns) in that plot suggest that the trends observed there are valid for all instruments.

7. “[...] At the moment the manuscript is rather a description of a characterization method for the instrument then a characterization of the instrument. Therefore it is well below its potential.”

The revised manuscript has de-emphasized the instrument-specific characterization and emphasized the Monte Carlo approach for single and multiple peaks. The new Fig. 10 presents generally applicable information. Quantitative estimates of peak-fitting imprecision must still be repeated for each new data set. We believe that the manuscript is much improved by these changes.

4 Specific Responses to Detailed Comments by Referee #2

1. “The method proposed for uncertainty estimation in routine data analysis so far is not really useable for routine analysis. For routine analysis this method should be included in PIKA.”

   It is planned to include this method in PIKA, but we avoid direct statements until the details become clear.

2. “P3473L7: Is it really errors in the m/z calibration which causes this kinds of uncertainty in the peak fitting or is it rather the behavior of individual ions, not agreeing with the m/z calibration or the limited number of points representing the individual peaks?”

   The statement on P3473L7 was made due to the results of the empirical analysis in Sections 3.4 and 3.5. The causes of errors in m/z calibration are not known, and their nature would not affect this statement.

3. “P3473L19: The constant relative imprecision in fitted peak height for isolated peaks was estimated as $\sim$ 4% and the overall peak-integration imprecision was approximately 5%. Does this make sense to spend so much effort on identifying the uncertainty of isolated peaks? As long as the background can be subtracted properly the area of individual peaks could be determined very reliably by adding the signals of all ions above threshold.”

   These may seem like tiny values, but as shown in Section 5, for high signals these percentages become much larger than the counting uncertainty which was previously considered the only source of imprecision. While the area of well-separated peaks can be determined by simple numerical integration, for peaks represented by a low number of data points this technique will also have its own uncertainties (which are likely to scale faster than $n^{0.5}$ for similar reasons as outlined in Section 2.3).

   Moreover, the uncertainty in isolated peaks was studied in order to understand the fundamental limitations and sensitivities which are important in the overlapping-peak case. The isolated-peak uncertainties presents a lower-limit for the overlapping peaks case, and since peak-fitting is a requirement for resolving overlapping peaks, this was an issue worth studying. We added a new figure to the manuscript (new Fig. 12) to illustrate when and why numerical integration is inadequate, as well as to demonstrate the application of the method proposed in the manuscript.

4. “P3474L3: The AMS provides rather semi-continuous measurements, not continuous ones.”

   We are not sure why the Referee considers the AMS semi-continuous (the frequent background measurements?) but we consider “continuous” to be more a appropriate description, especially in the context of the time resolution of other techniques in atmospheric science.

5. P474L8: Replace “external mixing state” by “mixing state”.

   The cited papers performed single particle measurements and report interesting results on externally-mixed PM.

6. “P3474L22: Thus PIKA only accounts for counting statistics errors. This could be stated here.”

   A good suggestion that we have incorporated.

7. “P3474L26: Can you specify “near that signal” further?”

   We intentionally did not specify this as “near” is given by a user-defined parameter, set by inspecting the mass spectrum. The basic SQUIRRREL/PIKA algorithm assigns $\pm 0.1 m/z$ as near, which is also based on inspection and mass-spectrometer resolution. We provide citations for the interested reader.

8. " P3475L21: Here you state that "bias" is an error of "constant value" and 2 lines below you state the PIKA integrations are "biased" by a "varying amount". This sounds like a contradiction. May be better make clear that biases don't average to zero."

This is an intentional contradiction and an important one. The manuscript discusses μ-prediction "biases" at length, and some scientists may think that these μ-prediction biases do not affect PMF since only imprecision matters there. However, if the bias during peak fitting is different between peaks, an imprecision in the entire data set will result. We have tried to clarify:

The distinction between these two concepts varies naturally at different stages of the analysis: if peak fitting is biased via a mechanism that varies from peak to peak, then an imprecision in the overall set of fitted peaks will result. As we discuss below, this is the case for PIKA fits to AMS data.

9. "P3476: I suggest putting the different kinds of errors into a more logical order: 1) instrumental, 2) counting, 3) analysis, 4) interpretation."

A valid suggestion, but we retain the current order, which is based on the ease with which the errors may be understood, and which leads naturally into the following discussion.

10. P3477L19: Replace ": : :, such those due : : :" by ": : :, such as those due : : :"

Thanks

11. P3478: A sketch describing the peak fitting with the relevant parameters and showing the uncertainties would be helpful.

A good idea which we have incorporated into the new Fig. 10.

12. P3478Eq(3): it would make sense to change the order of the two equations here.

We have adjusted this equation to better reflect the subsequent discussion.

13. P3478L20: Are these parameters constrained to certain fixed values or to ranges of values?

Please see P3478L21.

14. P3478L20: Are these parameters constrained to certain fixed values or to ranges of values?

The parameters are fixed at values defined from the calibrations, see P3478L16.

15. P3479L18: Add "is" between "calibration" and "determined".

Thanks

16. P3481L7: What is "AMS uncertainty"? Be more specific.

Thanks for pointing this out. Here it is the area, in units of counts, of the integrated peaks. We have updated the text.

17. P3484L7: It is unclear to me how this approach provides the information which is stated in the text.

The new introductory text to this section clarifies:

" The source of the constant relative RMSE in Fig. 2 was argued via Eq. 7 to be most likely due to errors in the predefined pseudo-Gaussian function f_0. To elucidate which of the parameters defining f_0 have the greatest impact on the errors of the resulting fit, imprecisions or biases were manually added to each of several input parameters in the PIKA analysis procedure as follows."

18. P3484L17: What does “large range of signals” mean – “large range of signal intensities”? What do you mean with “the behavior of all ions was similar”?

We changed:

This ion was chosen simply because it was observed over a large range of signals; the behaviour of all ions was similar.

...to...

This ion was chosen simply because it represented a large range of peak intensities (abscissa in Fig. 3); the trends seen in Fig. 3 were observed for all of the ions in Fig. 2 .

19. P3485L1-3: Not the absolute value of the errors needed to achieve this result is relevant but how large these errors need to be in relation to the errors occurring typically. Furthermore: is it really an uncertainty in m/z calibration or an error in identification of the peak location from the data with low number of data points on each peak?

First comment: Indeed, our wording here absolutely did not convey the right meaning. We had investigated the trends in the data used to generate the peak shape function v for biases and imprecision and found that these were negligible.

This is now conveyed: *The relative μ-prediction errors necessary to achieve this $\sim$ 15% relative RMSE were 5–10-fold larger than typical μ-prediction errors; the errors in v necessary to achieve this $\sim$ 15% relative RMSE were two orders of magnitude larger than the maximum distance between the best estimate of v and the data used to derive it, which was 0.4%.*

Second comment: When peaks were later simulated on the same m/z axes as found in the actual data set, they could be fitted perfectly when their location was not constrained. As the location of peaks is not constrained during m/z calibration either, the issue cannot purely be the number of data points for each peak. That issue does however become important when doing location-constrained fits.

20. P3485L9-10: Why could the peak shape not be meaningfully varied? Different m/z could be used to determine peak shape.

All isolated ions are normally used to determine the peak shape, and we have never observed significant deviations which were not due to statistical noise or peak overlap. Variation would have to come from sampling the peak shape of many AMS's with their various tunings and other details.

21. P3485L12-14: Again: is it really imprecision and bias in m/z calibration or is it that individual ions have certain deviation from this calibration? If the calibration is really biased and such measurements as shown here can determine this bias it should be possible to use these measurements to determine an unbiased m/z calibration. It would be interesting if an improved m/z calibration (using the results presented here) would also improve the peak position-related uncertainty for peaks not used for this calibration. If the reason for this kind of error is really the imprecise m/z calibration this calibration should improve this way and this should reduce the peak position-related error and as a consequence the overall uncertainty of the analysis!

It is possible to modify the calibration equation to account for deviations from the theoretical equation, as now discussed in Section 6. This can significantly reduce m/z calibration biases, but each modification typically consumes an extra degree of freedom. Reliable and robust calibrant peaks are then needed, and these are not always available. Including low-signal-to-noise peaks in the calibration can significantly reduce its accuracy (Cubison and Jimenez, ACP 2015). Even if biases are reduced, they must be subsequently evaluated to estimate their significance.

Section 6.2 went into more detail on the potential for improving the m/z calibration. The ideal solution would be to have an internal calibrant in every mass spectrum, in a manner that did not interfere with the samples. This is impractical. Another ideal solution would be to have high enough resolution that the peaks of interest do not overlap and could be numerically integrated. This is unlikely, since ions of atmospheric interest can have extremely similar m/z. We hope that the issues outlined in this manuscript might motivate a practical experimental or alternative solution in the future.

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