

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

**Anonymous Referee #2**

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In their manuscript “Peak fitting and integration uncertainties for the Aerodyne Aerosol Mass Spectrometer” J.C. Corbin and coworkers present a detailed analysis of uncertainties related to the analysis of high-resolution mass spectra from the Aerodyne Aerosol Mass Spectrometer. Besides a general discussion of sources of uncertainty of high resolution data, the manuscript focuses on uncertainties related to imperfect fitting of the high-resolution peaks. Major sources of uncertainty were found to be from uncertainty in peak position likely due to imperfect  $m/z$  calibration and from differences in assumed and actually measured peak shape. For isolated peaks the uncertainty due to peak position uncertainties has been found to be in the order of 4% and the uncertainty due to peak width in the order of 2.5%. This results in an overall uncertainty from the analysis in the order of 5%. For adjacent peaks an additional uncertainty was

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observed which is larger the less separated the peaks are. For sufficiently small peak distances this additional uncertainty increases up to 100%. For peaks of different intensity the smaller peak is more prone to such effects than the larger one. 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

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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.

General comments:

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

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.

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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?

The  $m/z$  calibration seems to be the most critical factor for the analysis uncertainty. How can this calibration be improved? Alternatively, 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, ...)? This might be possible to test by including the peak positions from Figure 5 into the  $m/z$  calibration. If it is possible to generate a common calibration which improves the uncertainties in peak position for all these signals at the same time this would point towards an un-perfect  $m/z$  calibration. If this is not possible this points more towards other effects causing individual ions to deviate from the calibration.

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 and the user could find the uncertainty (or even uncertainties for final AMS products like species concentrations, H:C, O:C, N:C ratios, ...) for the “own” instrument. At the moment the manuscript is rather a description of a characterization method for the instrument than a characterization of the instrument. Therefore it is well below its potential.

I think the result that the analysis-related uncertainties mostly scale linearly with peak intensity is a very important finding which is very relevant for PMF analysis and should be stressed more than it is at the moment.

Detailed comments:

P3473L5: This manuscript does not only evaluate the significance of these uncertain-

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ties but also the magnitude and dependences. 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.

P3473L7ff: 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?

P3473L19ff: The constant relative imprecision in fitted peak height for isolated peaks was estimated as ~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.

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

P474L8: Replace "external mixing state" by "mixing state".

P3474L22f: Thus PIKA only accounts for counting statistics errors. This could be stated here.

P3474L26: Can you specify "near that signal" further?

P3475L21ff: 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.

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

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

P3478: A sketch describing the peak fitting with the relevant parameters and showing

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the uncertainties would be helpful.

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

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

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

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

P3484L7ff: It is unclear to me how this approach provides the information which is stated in the text.

P3484L17f: What does "large range of signals" mean – "large range of signal intensities"? What do you mean with "the behavior of all ions was similar"?

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?

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

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!

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P3486L23ff: If the mean of aggregated  $e(\mu)$  is zero – as stated here – doesn't this suggest that there is no systematic error in m/z calibration?

P3487L6: Are observed deviations from m/z calibration from non-idealities in the ion trajectories within the mass spectrometer or within the ion source (e.g. different ions preferentially originating at different locations in the ion source)? Are these biases you observed specific for the individual ions (i.e. the same for other instruments), are they specific for the instrument you used, are they constant over time? Is it possible to calibrate for them?

P3487L17ff: Please make clearer what this Monte-Carlo model is needed and useful for.

P3489L20-23: in line 22 add "m/z" before "resolution". Does it really make sense to reduce m/z resolution to obtain more data points on each peak for reduced fitting imprecision? Would this not be more than outweighed by increased overlap imprecision?

P3490L5-7: Why can the other peaks not be investigated?

P3490L17: Add "of the individual ion signals" after "that the peak shape".

P3491L14: Why should the  $e\mu$  for each peak in a set of overlapping peaks be equal? If the reason for the deviation from the m/z calibration is not m/z dependent but depends on the type of the ion this is not necessarily the case.

P3492L4ff: This result rather points towards a source for the  $\mu$ -error which is not a function of m/z.

P3493L4f: The error for equally high peaks does not begin to increase at about 1 SD but it increases for distances less than 1 SD (while one could also state that it increases for distances less than 2 SD). It would be interesting to add the typical error for isolated peaks to Figure 9 for comparison.

P3494L1: Add "ppm" after the value in parentheses.

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P3494L14: Add "be" after "if it is to".

P3494L20ff: This is rather unsatisfactory. The user wants to know the errors made in the analysis. This sounds rather complex. How well do you expect the resulting errors to be obtained?

P3495L4f: Add "of adjacent peaks" (or something similar) after "due to overlap".

P3495L12: Make clear, that this is the uncertainty for isolated peaks only – which is rather the exception than the rule.

P3495L21: Why is the asymptotic value in Figure 11b 1.8% and not 4.7% as claimed in equation (12) ?

P3496L2f: At least an estimate of how much these imprecisions and biases vary for other instruments would be important for other AMS users.

P3496L13: Replace "different workers" by "other groups".

P3496L16-19: Be more specific here: What is influenced and how?

P3496L21ff: There is no information given about how well your approach works for more than two peaks overlapping. In addition, since no estimate for real peaks (with reasonable mass resolution and known peak separations for typical AMS) is provided, this approach is only of limited use for the AMS user. It rather shows the user a possible approach how to estimate uncertainties.

P3497L6ff: Would it help to also fit the peak position to reduce uncertainty? Would this be possible for multiple overlapping peaks if only reasonable ranges would be allowed?

P3498L22: This uncertainty of 20% of single-ion signal intensity seems to be much more severe than the peak fitting uncertainties of 2-4%, especially if the uncertainties due to overlap are not accounted for. I am wondering whether determining the uncertainty of peak fitting is worth the effort if it excludes probably the largest fraction of the peak fitting uncertainty and at the same time contributes almost negligibly to the overall

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uncertainty of AMS measurements.

P3498L25f: What kind of hardware improvement is meant here?

P3498L27f: Since isotopes are not from a process where one isotope is the result of a decay of the other one I wonder whether it is correct to call isotopes “daughter-“ and “mother-“ ions.

Section 6.4 – Other sources of uncertainty: Since there are so many potentially more important uncertainties in AMS measurements compared to peak fitting uncertainties (at least for isolated peaks) it might be sufficient for the user to know the approximate uncertainties due to fitting and the limits where these uncertainties increase significantly (e.g. for peaks with little separation).

P3499L10-15: This is really important! This might result in the need of changing how uncertainties for PMF matrices are calculated and could significantly impact the associated results. It would be desirable if this would be discussed a bit further, including a discussion which signals are typically subject to such over-weighting which is not addressed by the current error definition. By how much can the user expect the PMF results to be uncertain or biased due to this effect? At least an estimate of such uncertainties would be highly desirable.

P3501L14: Since area is typically not measured in kHz, this statement might be confusing.

P3501L18: “significantly” needs to be “significant”

Conclusions section: I think the important impact of your findings on potential PMF uncertainties should be included in the conclusion. Furthermore the mass concentration ranges and m/z where all these effects become really significant should be mentioned here.

P3502L9: “wood aerosols” should be “wood combustion aerosols”

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Table A1: Instead of “in imprecision” it would help if you would name the individual types of imprecisions which you use in this manuscript.

Figure 2: Why are the RMSE data points systematically larger than the fit line for large peak heights? Is there an additional source of uncertainty or a bias?

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Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3471, 2015.

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