

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

Anonymous Referee #1

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Corbin et al. present a novel estimation of the errors associated with the peak heights as calculated by a constrained peak-fitting procedure heavily employed by the atmospheric community, in particular here motivated by the Aerodyne Aerosol Mass Spectrometer. These errors have been poorly treated in the literature and their work is to be welcomed. They do a good job of presenting what is clearly a complex topic. They present test cases to demonstrate and explain an important source of error in their fitting parameters. However, they go on to extrapolate from these test cases to the generalized situation without adequately supporting their methodology and/or assumptions. This must be addressed before the study can be considered for publication. If these issues can be resolved then their simple formulation for an error estimation would be a useful result.

MAJOR POINT 1: Demonstrating magnitude of linear error term in the general case.

In Figure 6 and associated discussion, the authors neatly show that a bias in the m/z calibration for a given, known, peak leads to an error in fitted peak height that scales linearly with height. The data points agree with simulations performed incorporating this bias, thus backing up their statement about the source of the error (as is also well-argued in the discussion surrounding Figs 3 and 4).

They go on to perform similar simulations for a set of known peaks: In Figure 5, they show that the m/z biases for each of their test ions are different, which impacts the distributions shown in Figure 7 (following from the discussion in 3.6 that the biases impact the imprecision). In order to make their generalization that σ_h is a fixed fraction of height for all ions (not just the test case), they are assuming that this error scales similarly with peak height for all ions irrespective of the m/z bias to which they are subjected. The similar slopes in Fig 2. are meant to support this theory (line 25 p3483). The authors ought show the mean simulated lines of “Fit RMSE vs peak height” for all 7 test ions (like the white line in Fig 6., but with different colors for the different ions) to support this statement. In the event that this slope is identical for all ions, perhaps they might discuss why this is the case, as this generalization is an important part of their conclusions, both here and in the final concluding remarks.

Furthermore, at the end of section 3.8 when estimating the magnitude of peak-fitting imprecision σ_h , it seems like the distributions used to derive the 2% value quoted are taken from Fig. 7, which presumably don't include the biases as (line 18 p3488 “mean fitting error (bias) has been subtracted”). If my interpretation of Fig. 6 is correct, the bias leads to the observed slope and the imprecision (broadened by the slope effects mentioned in 3.6) is the spread in light blue around this line. Therefore using Fig 7, which is considering only the imprecision, to i) estimate their magnitude and ii) demonstrate that this magnitude is generally applicable appears false. Surely if there were no bias, the σ_h imprecision distribution would stay constant as in the noise region for low signal and thus not scale linearly with h ? It follows that the important

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parameter determining the magnitude of the linear increase in σ_h with h is the bias and that the imprecision distribution is largely irrelevant.

At present, the “~ 4%” quoted on line 6 of p3495 is simply not supported. At the very least the data for all test ions must be presented. A better approach would be to simulate their calibration routine and evaluate the biases for every significant ion across the entire mass spectrum. My principal concern is that, since they show some ions have positive and some negative m/z biases, there must presumably be cases where an ion has no bias at all. The application of a linear error term in this instance would be a gross overestimate of the error, as I'd expect to see a zero slope in a similar plot to Fig 6. If this is wrong, the authors must demonstrate it. If this is correct, then the range of biases must be considered when applying the linear error term.

In summary, the authors have shown that, for their test peak, a linear fit RMSE (~5% of h it seems) fits modeled and real data. But in the generalized case, they have not shown how this linear relationship varies for ions across the mass spectrum, and therefore that it is applicable generally. They also need to clarify how they arrive at the values for σ_h presented and demonstrate how this is related to the measured/modeled biases.

MAJOR POINT 2 : Application of the linear error term for multiple, overlapping, peaks

The application of the aforementioned linear error term together with an “overlapping-peak scaling parameter”, b , presented in Eqn 11 is perhaps the most important result presented in this paper. If this can be justified, it would allow for a simple, quick, estimation of fit errors for complicated fitting scenarios (for the somewhat constrained fitting technique used by the PIKA software utilized in this study). However, its application is based on the false assumptions that i) the fitting errors will symmetrically increase/decrease as the m/z calibration is perturbed, and ii) the m/z bias for a given peak is known.

In the final remarks of section 4.3, the technique for assessing b for a given set of

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ions in an overlapping peak fit is presented (incidentally, it took me quite some time to understand this, perhaps clarify the discussion). The concept is to utilize the known peak separations together with fitted peak heights and an estimated, fixed, value of m/z calibration error (10 ppm? - it's not clear what is appropriate) to simulate the CHANGE in peak heights as compared to the perfectly calibrated case (the ratio is b). If this is wrong, then the authors need to simplify and re-phrase their discussion!

Assessment of b is however difficult. Changing the calibration by + 10 ppm will not necessarily change the peak height by the same magnitude as by - 10 ppm (following the discussion in sect 3.8), so how is this taken into account? Furthermore, it is shown in Fig. 5 that the m/z bias for different ions is not the same, indeed the average of all peaks looks like it has a zero bias, which the authors indeed report on line 24 page 3486. So how do the authors know what the “realistic u prediction errors” (line 24, page 3494) are? Currently, the condensation of all these effects into a single scalar is described by on line 5, page 3495 as “as described in Sect. 4”. This is vastly insufficient. The authors themselves state on line 25 of 3489 that “These seven peaks present a very limited sample, and are unlikely to adequately represent the following important uncertainty.”

A programmer might be able to understand the methods from their code (the authors are commended that they make the software available upon request), but at a minimum a flowchart should be provided in supplementary info. and the equations that directly lead to the calculation of b from the peak heights presented in the main paper. These must include the dependencies on the magnitudes of the u prediction errors, which must in turn be justified with reference to Fig. 5. Asymmetries must be addressed. This is very important in order to justify this important generalization.

Finally, do the authors believe this estimate represents a min/max/best estimate of the peak fitting errors?

MAJOR POINT 3 Can the authors provide example graphics of the results discussed in

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the discussion following from line 26 p3489 “following exploratory data simulation. . .”? How does the magnitude of the u prediction error depend on the number of data points comprising the peak? At present, this is somewhat qualitatively taken into account in the final sentence of sect 3.8. This isn’t sufficient, the absolute magnitude of the σ_h is of direct consequence to the estimations of error presented in the concluding sect 5. Therefore it is important, if the authors believe they have shown sensitivities in simulations, to quantitatively account for them, or disregard them as negligible as appropriate. Simply doubling the estimate without presenting any supporting data is incorrect.

OTHER COMMENTS

Minor point 1: I am a little unclear as to what is presented here. The data are from fits to the same mass spectrum, so each data point is a different Δu ? The noise presumably arises from the use of real data, would it not be better to use simulated peaks as indeed the authors do elsewhere? Then perhaps the effect of the detector bins mentioned on line 6 p3492 would be easier to assess.

Minor point 2: In sec 4.2, (line 22 p3492) the use of counting error in the modeling of multiple peaks is explicitly removed. I realize this must be to concentrate on the effect of the m/z calibration in the results since that is the thrust of this study. Perhaps the authors might mention what influence this would be expected to have? Does it change the shape of the curves at all, was this modeled? If so, a supplementary figure to demonstrate that it doesn’t impact the findings with respect to the u prediction biases would be useful.

Minor point 3: In 6.3 line 30 p3498 it is noted that the signal intensity of a single ion varied by $\sim 20\%$. Does this impact the shape of the mass spectra utilized in this study and therefore could it play a role like is assumed for the detector bin spacing?

Minor point 4: Line 14 p3501 Does 1 kHz mean 1000 ions arriving at the detector in one second? This unit is often seen in AMS-related publications but it seems a little

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confusing as one usually associates it with wave frequencies.

Minor point 5: In the modeled data of sec 3.7, the u constraints are taken from the mean and SD value of Fig. 5 (line 28 p3487). It is not stated if the mean and SD are taken on an ion-per-ion basis, or using the distribution for all ions. Please clarify (I'm assuming ion-per-ion). What is the effect if the ion-per-ion or all case (ie, opposite to that used) is taken instead? How does that influence Figure 6? This would be important for discerning between the ion-specific and generalized case.

Minor point 6: On line 18 of p3488 it is mentioned that the "mean fitting error has been subtracted". This is not clear. One assumes this means the distributions are shifted in x, otherwise the distribution for the ion used in Fig. 6 ought be centered around 5% as the slope of Fig. 6 would suggest. Both distributions (with and without bias) should be plotted in Fig. 7.

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