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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Applications and limitations of constrained high-resolution peak fitting on low resolving power mass spectra from the ToF-ACSM" *by* H. Timonen et al.

Anonymous Referee #3

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General comments

The manuscript describes a way to extract the signal of selected ions from an Aerodyne TOF-ACSM whose signals are disturbed by isobaric ions. This is done by fitting peaks with a custom shape to the expected isobaric ions. Since the position and the shape of the peaks are known, the only parameters to be fitted are the heights of the peaks. The results are used to calculate refined time series of selected compounds. An important feature of the publication is the discussion of the sensitivity of the results to uncertainties in the mass calibration, which covers the influence of counting statistics and isobaric ions. Furthermore the limitations of the method with respect to the compounds that can be analyzed are presented as well as techniques to evaluate the

quality of the results. This is very important to allow other users to use the method appropriately.

An important factor that is not covered is the influence of the peak shape on the results. The authors assume a fixed peak shape without showing that the peak shape is really constant over the whole spectrum, nor do they show that the influence of an instability of the peak shape is not relevant to the results. A possible analysis for the sensitivity to the peak shape would be to split the mass spectrum into two sections A and B and determine the peak shape for these sections separately. The different peak shapes could be compared to determine how stable the peak shape actually is. In a second step, the peak shape of section A could be used to perform the deconvolution for an ion signal in section B. The resulting time series could be compared to those using the peak shape of section B.

What is also missing is a real comparison of the results from the deconvolution of the low resolution spectra to the results from a HR-TOF-AMS. Such a comparison could be used to directly validate the results from the presented method. The presented examples, although very useful to understand how to properly apply the method, only show that the results are plausible. A comparison to high resolution data would directly reveal the quality of the deconvolution. (See specific comments)

As a technical paper in the field of aerosol science, the paper fits well in the journal Atmospheric Measurement Techniques and I recommend to accept the manuscript for publication after addressing the influence of the peak shape and after adding a comparison to a HR-TOF-AMS.

Specific comments:

3.1.1 The baseline calculation assumes that the baseline is always reached between peaks. This is surely not the case at high m/z. Although this is not relevant in the mass to charge range covered in the manuscript, it might be worth noting when the method is described.

3.1.2.2 This section completely relies on the peak shape being constant over the whole mass range. I doubt that this is the case, especially when looking at Fig. S11. This fit clearly shows that the peak shape does not well represent the peak shape of the signals at this mass. The left region of the fit is significantly different from the fitted curve.

3.2 A short comment on why the spectrometer resolving power, although being an intrinsic limitation of the hardware, does not need to be considered would be helpful. It would be beneficial to know to what extend this could influence the result, even if it possibly just means stating that it is irrelevant compared to other influences.

3.2.2.2 Please explain what is meant by “background peaks”. It can only be deduced later from the text that it must be the signal on the mass to charge ratios surrounding the calibrant ion signal.

3.2.4 This is de facto an addition of more parameters to the mass calibration.

3.3 The parameterization of Cubison and Jimenez (2015) assumes the ideal case of a constant peak shape. This is not the case here. “Imprecision in such a constrained fitting procedure may arise from . . . (iv) the instrument transfer function (“peak shape”). . . . Since the errors from iv are not included, our results represent a best-case scenario for the precision of the retrieved parameters.“ (Cubison and Jimenez (2015)) Please add the information that the parameterization represents a best case scenario.

4.2 Figure 11 shows the time series of the results of the separated ion signals. On the left, the unperturbed fitted signals are compared to the full signals and it is noted that the total signal is well reproduced by the best fit. How does this look like for the perturbed case? Is the reproduction of the total signal by the separated signals much worse in this case? This would be a good indication that the comparison to the total signal is actually sensitive to poor deconvolution of the isobaric ion signals. Such a graph would be nice in the supplemental.

4.8 Second paragraph: Using a transfer function to convert HR-TOF-AMS fitted spectra to ETOF spectra is not a valid verification of the method. The fixed transfer function implicitly adds the assumption that the shape of the peaks is constant. However, this is an assumptions that needs to be verified.

Technical corrections: p2 l2: Atmospheric aerosols p2 l16: better: in literature p3 l22: Why did you assume a collection efficiency of 0.5? p6 l29: an imperfect mass calibration Table 4: Sensitivity (without -)

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