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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 #2

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The manuscript describes in detail the methodology used for separation of isobaric ions using constrained peak-fitting in data from the ToF-ACSM and thoroughly discusses good practices and limitations of the procedures applying them to three datasets recorded in different environments. The manuscript is well written and structured, and it falls within the journal's main subject area "validation of measurement techniques". I recommend the publication of the manuscript in AMT, after addressing the following issues:

GENERAL COMMENTS

The manuscript could be more specific on the advantages of the methodology with respect to using the unit mass data together with the fragmentation pattern in order

to determine mass concentrations. The manuscript spends several pages discussing the application of the peak-fitting to ammonium, nitrate and sulphate ions, concluding that it is not possible to deconvolve the ammonium ions and that it is possible to do it with the sulphate and nitrate ions; the implications or importance of this conclusion are not explained. On the other hand, the cases for which the peak-fitting represents a real advantage (HOA/OOA constants and the oxidation state) are not as thoroughly explained and discussed.

SPECIFIC COMMENTS

SECTION 3.2.4. The discussion in this section is very vague. The bias described in this section, as well as the methodology to compensate for it should be explained in more detail for the benefit of the reader. Several questions remain unanswered after reading the section. For example: a) "In certain cases, a bias exists in the mass calibration fit residuals...". Which cases? How often is this bias observed? Why is this effect observed? b) "...apparent polynomial shape in mass-to-charge space, as exemplified in Fig. 8." How many terms did the polynomial used have? How was the number of terms chosen? c) "A MS with known calibrant ions in the central mass range exhibiting strong mass spectral peaks can thus be used to minimize the residuals, and this subtraction applied to all calibrations in the entire dataset time-series". Which subtraction is this paragraph referring to? How is the subtraction performed?

SECTION 4.2 (Nitrate) Compare mass concentration results using the integrated data together with fragmentation table vs. the peak-fitting, as it was done for sulphate.

PAGE 20, LINE 20. "Stark et al. used the 20 higher mass resolving power of their data together with comprehensive ion lists to analyse the mass excess of all the fitted ions using the constrained peak-fitting methods described in section 3. A mass resolving power of ~ 500 precludes this approach, so instead, the simpler bulk mass spectrum method also proposed by Stark et al. was employed." It is not clear what is the difference between the method originally used by Stark et al., and the simpler method used

for this work. Can the authors better explain it?